– Coordination Compounds –
(or Complex Compounds)

Classification of Salts :-

(1.) Simple Salt :
→ Consists of only one type of cation and anion.
eg. NaCl, $BaSO_4$, $CaCl_2$, Na_2CO_3 etc.

(2) Mixed Salt :
→ Salts having either more than one type of cation or more than one type of anion.
eg. Bleaching Powder ($CaOCl_2$)

$\Downarrow$

Ca^{2+} Cl^- } OCl^-

↑
Bleaching action is due to oxidizing nature of OCl^- (Hypochlorite ion)

eg. Microcosmic Salt,
$Na(NH_4)HPO_4 \cdot 4H_2O$ (Used in qualitative analysis in phosphate bead test)

$\Downarrow$

Na^+, NH_4^+ } HPO_4^{2-}

(3) Double Salt :

→ It is combination of two simple salts in a definite molar ratio.
eg. Potash alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$)
eg. Mohr Salt : $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
eg. Carnallite ore : $KCl \cdot MgCl_2 \cdot 6H_2O$

⇒ Potash alum (a double salt) can be obtained when aqueous solution of K_2SO_4 and $Al_2(SO_4)_3$ are mixed in 1:1 molar ratio and evaporated to dyn. dryness.
Residue obtained is Potash Alum.

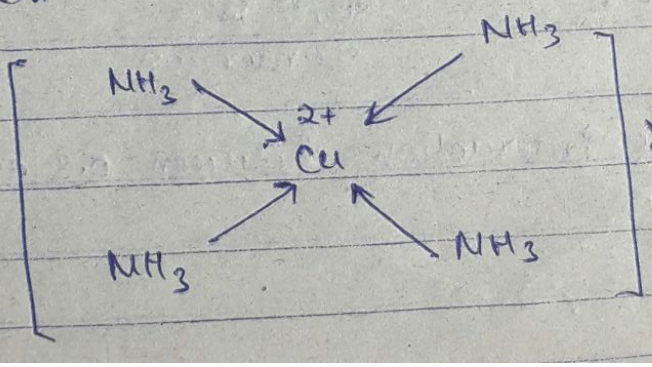
imp NOTE Aq. solution of double salt gives qualitative tests of all ions of salt.

eg. aq. soln of potash alum gives qualitative tests of K^+, SO_4^{2-}, Al^{3+}
(Such property is not shown by complex salts or coordination compounds).

(4) Coordination Compound (or) Complex Salt :
It consists of central atom/ion (usually a metal atom) attached with definite no. of species (called ligands) through coordinate bonds.

eg. $CuSO_4(aq)$ + $NH_3(g)$ $\longrightarrow$ $[Cu(NH_3)_4]SO_{4(aq)}$
Blue soln
Deep Blue soln.
Complex Salt.

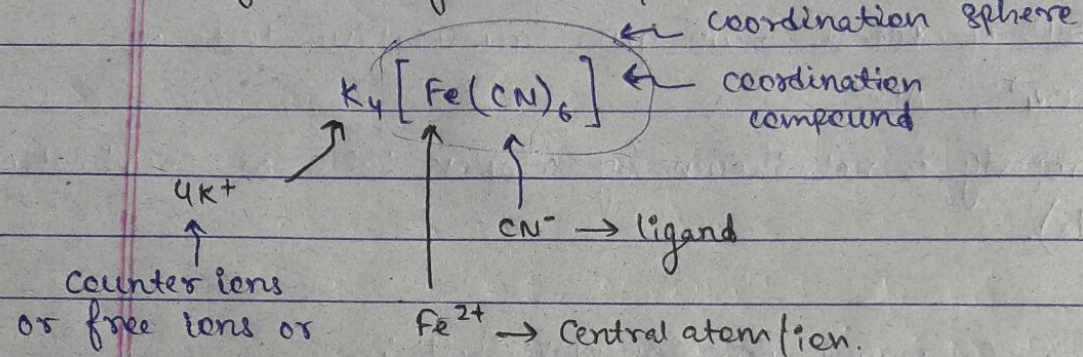
$[Cu(NH_3)_4]SO_4$
Central atom
4 NH_3 are called ligand.



NOTE An aq. soln of $[Cu(NH_3)_4]SO_4$ does not give qualitative test of Cu^{2+} as Cu^{2+} is not freely available in the solution.

Infact, it gives test of SO_4^{2-} and $[Cu(NH_3)_4]^{2+}$

(*) Definitions of some important terms :



(1.) Coordination Sphere / Coordination Entity :

It consists of all ligands and central atom(s)

→ Square bracket is used to show coordination sphere.

(2) Ionisation Sphere (or counter ions or free ions)

Part of coordination compound other than coordination sphere.

eg. $[Fe(H_2O)_5(NO^+)]SO_4$

C.S

SO_4^{2-} is counter ion.

→ There is an Ionic interaction between C.S and counter ion.

③ Central Atom :

Usually a metal atom of small size (mostly of d-block metals and small sized 's' and p-block metals) and also some less EN non-metals and metalloids.
(eg. B, Si, Br etc)

→ Central atom accept L.P of electron (or π-electrons in some cases) from ligand and hence central atom act as Lewis Acid

eg. of Central Atom :

Metals → Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ag^{+}, Au^{3+}, Zn^{2+}, Cd^{2+}, Li^{+}, Be^{2+}, Mg^{2+}.

→ Non metals : B, Br, Si etc.

eg. $[BF_4^-]$, $[BrF_4^-]$, $[SiF_6]^{2-}$

* Ligand :

A neutral or anionic or rarely cationic species which donate L.P of e^- (or π-e^- density) to central atom in a definite geometric arrangement in coordination sphere.

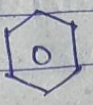
→ ligands form coordinate bond by donating L.P to central atom (in most cases). So ligands act as Lewis Base.

* Every Lewis Base can act as ligand, But Every ligand is not a Lewis Base.

eg. of Ligand which donate L.P

X^- (F^-, Cl^-, Br^-, I^-), $H_2\ddot{O}$, $N\ddot{H}_3$, OH^-, NH_2^-, NH^{2-}, en, PH_3, PPh_3, CO, CN^-, OCN^-, SCN^- etc.

eg. of ligands which donate π - electron density

C_2H_4,  ,

Ethylene Benzene Cyclopentadienyl ion.

Density Denticity and Chelation:
(Properties of ligand)

→ Denticity of ligand :-

It is the no. of σ - coordinate bonds formed by a ligand with same central atom.

eg. Denticity = 1, Monodentate ligand
= 2, Didentate ligand or Bidentate
= 3, Tridentate or terdentate ligand.

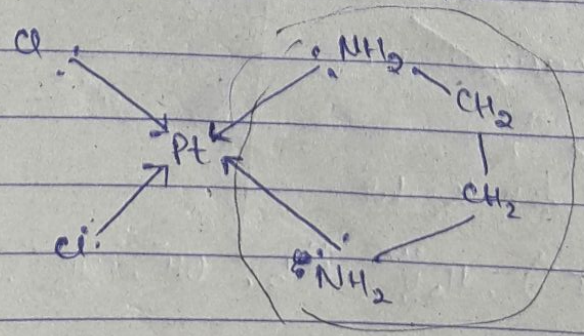
→ Chelation:

When a bidentate or a polydentate ligand forms a ring with central atom, the phenomenon is called chelation and ring formed is called chelating ring.
Such ligand is called chelating ligand.

eg. Ethylene diamine, $\ddot{N}H_2CH_2CH_2\ddot{N}H_2$

eg. $[PtCl_2(en)]$

↳ square planar complex



Chelating Ring.

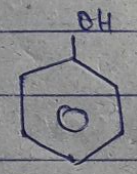
→ Chelation provides stability to the complex.
(Chelation effect)

eg. of monodentate ligands :

eg. X^- (F^-, Cl^-, Br^-, I^-), H_2O, OH^-, NH_3, NH_2^-, NH^{2-}

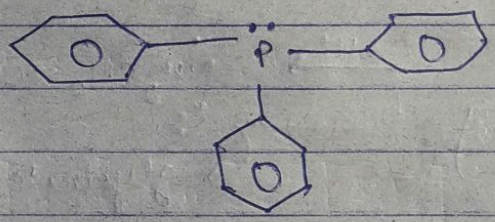
NH_2^- : amide ion
NH^{2-} : imide ion.

N_3^- (azide ion), CO, CN^-

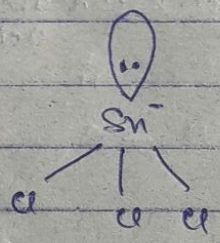


Phenol

$\ddot{P}H_3$, $\ddot{P}Ph_3$ (Triphenyl phosphene)

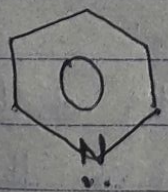


$\ddot{S}nCl_3^-$ (Trichlorostannate ion)



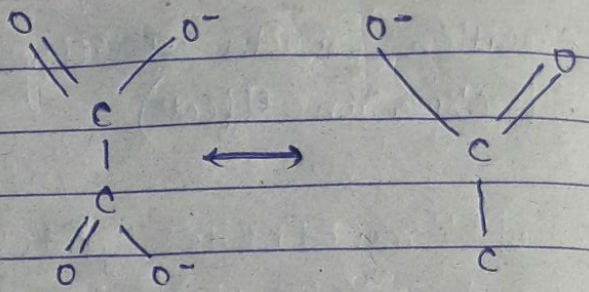
OCN^-, NCO^-, NO_2^-, ONO^-

* NO_2^- can act as monodentate as well as bidentate ligands.

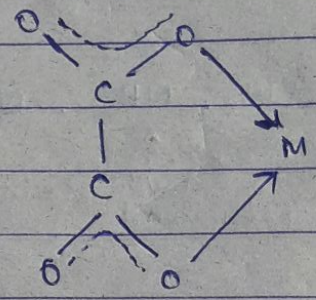


Pyridine (Py)

eg. Oxalate (O_2^{2-}) : (Symmetrical)



Resonating Structure



Chelating Ring.

(5 or six membered chelating rings make the complex highly stable.)

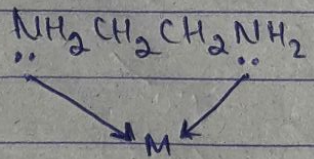
Imp eg. Glycinate ion (gly^-) : (Unsymmetrical) { Bidentate monoanionic ligand }

$NH_2CH_2COOH \xrightarrow{-H^+} NH_2CH_2COO^-$

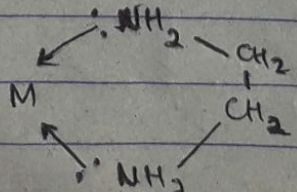
Glycine (an amino acid) → Glycinate ion (gly^-)

* one 'N' one 'O' are donor atom.

Imp eg. Ethylene diamine (en) :



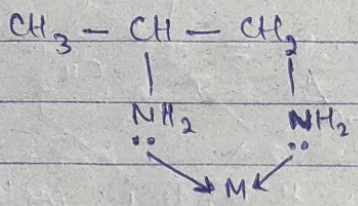
→ To act as a bidentate or a polydentate ligand their should be proper orientation of donor atoms so that L.P can be donated to central atom.



* Azide ion (N_3^-) can't act as bidentate ligand

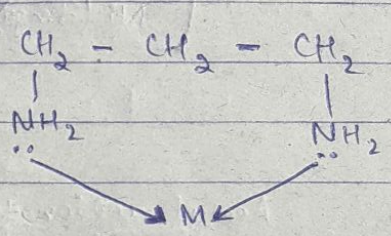
$:\ddot{N}^- = N = \ddot{N}:^-$ (behaves as monodentate ligand)

eg. Pn (propylene diamine):



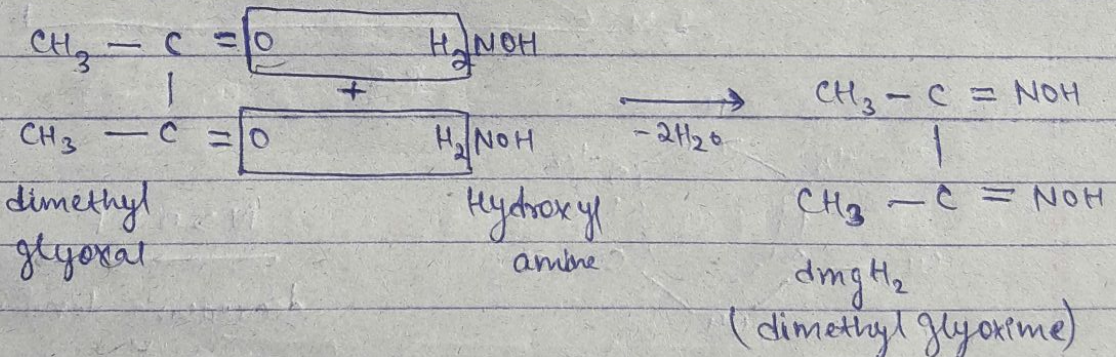
{M → Central atom}

eg. tn (trimethylene diamine):



v. dmg

eg. dimethyl glyoximate ion (dmg or $dmgH^-$)
(Unsymmetrical)

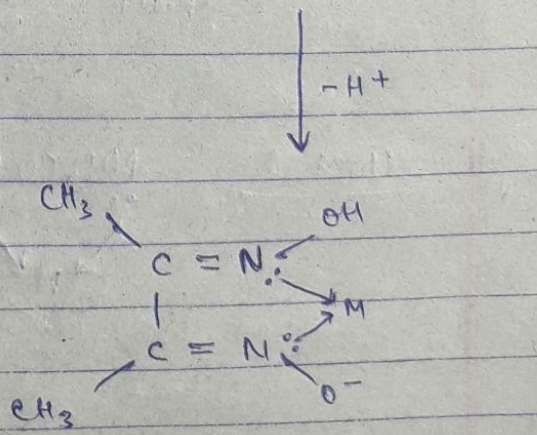


dimethyl glyoxal

Hydroxyl amine

$dmgH_2$ (dimethyl glyoxime)

* Both 'N' atom are donor atoms in $dmgH^-$

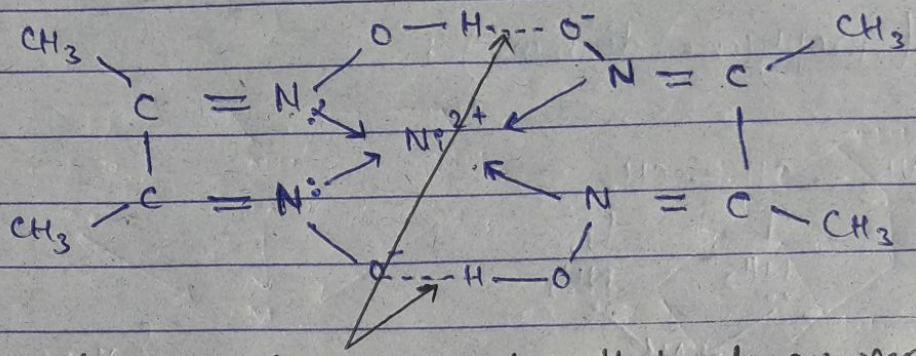


$dmgH^-$ (dimethylglyoximate ion)

V.V. Imp

eg. $[Ni(dmg)_2]_{(s)}$ (or) $[Ni(dmgH)_2]_{(s)}$

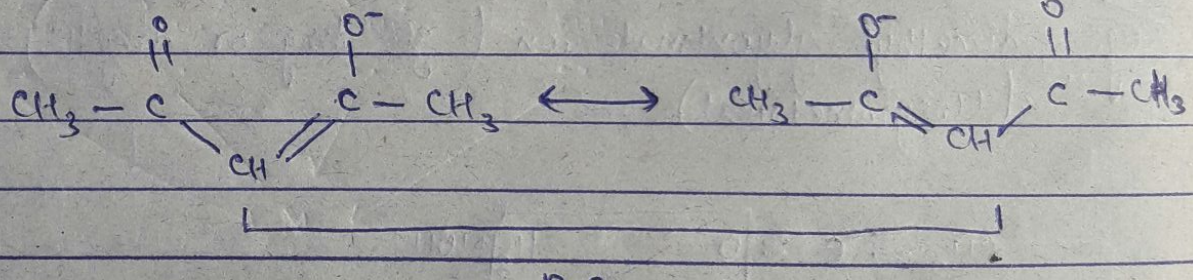
↳ Rosy red ppt.



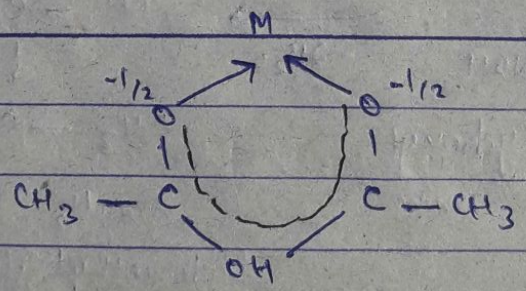
Two intramolecular H-bonds per molecule.

$[Ni(dmgH)_2]$

eg. Acetyl acetonate ion ($acac^-$) :



R.S



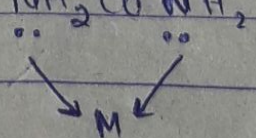
(R.H)

$N > O > F$

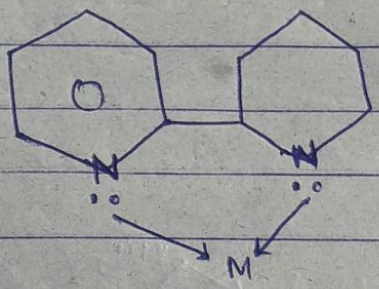
decreasing tendency to donate L.P

(E.N ↓, e- donating tendency ↑)

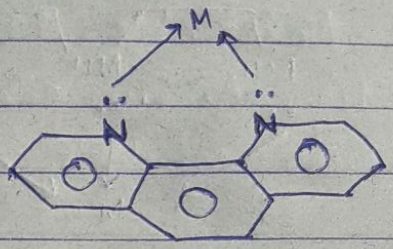
eg. Urea :



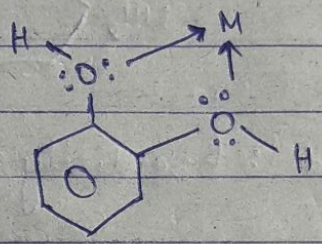
eg. dipy or bipy (dipyridyl or bipyridyl)



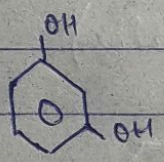
eg. o- phenanthrolene (Phen)



eg. Cathecol,



* Resorcinol,

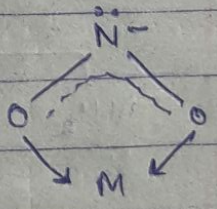


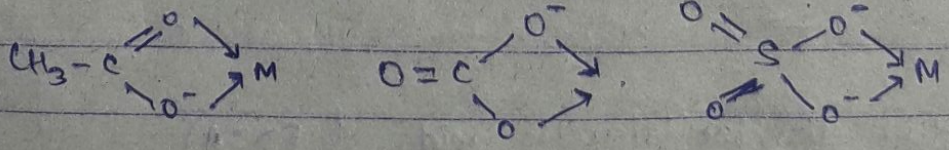
and quinol

can't act as bidentate ligand.
(However they may act as monodentate ligand)

NOTE: Some ligands show different denticity in different complexes, known as flexidentate ligand.

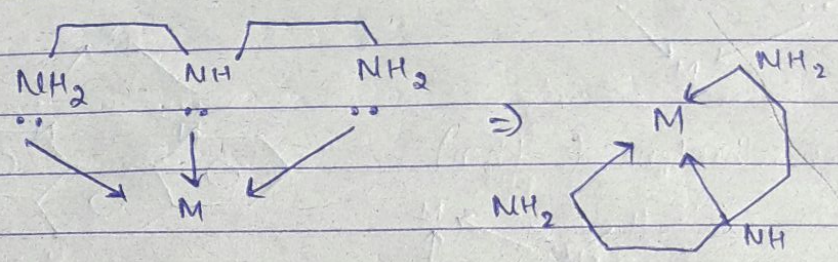
eg. CH_3COO^-, CO_3^{2-}, SO_4^{2-}, NO_2^- ⟶





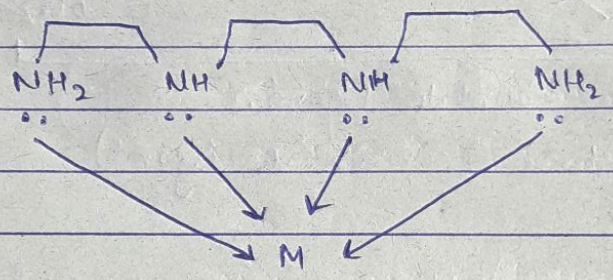
eg. of terdentate (or tridentate ligand):
(denticity = 3)

eg. dien (diethylene triamine)



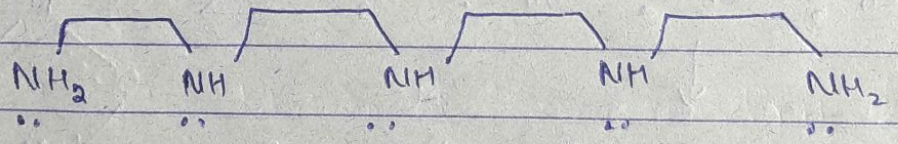
eg. of tetradentate ligand : (Denticity = 4)

trien (triethylene tetraamine)

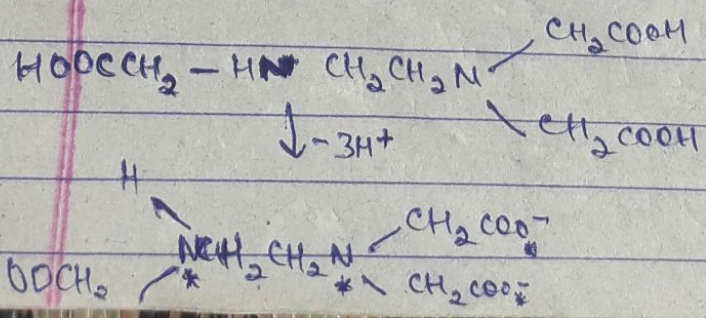


eg. (a) of pentadentate ligand : (Denticity = 5)

tetraen (tetraethylene pentaamine)



eg. (b) Ethylene diamine triacetic acid (EDTA)



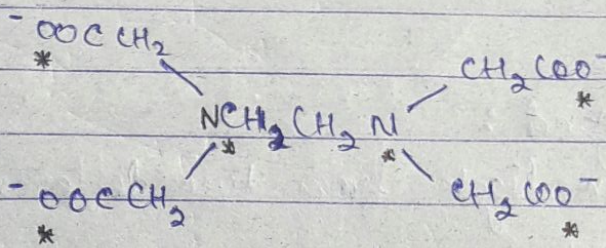
'*' represents donor atoms

(2N 3O are donor atoms)

V. imp

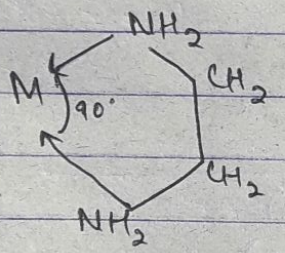
eg. of Hexadentate ligand :

eg. $EDTA^{4-}$ {Ethylenediamine tetraacetate ion}

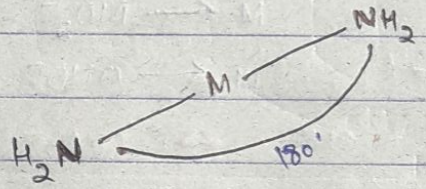


(2'N' and 4'O' are donor atoms)

(*) Two adjacent donor of a polydentate ligand occupy cis-position with central atom.

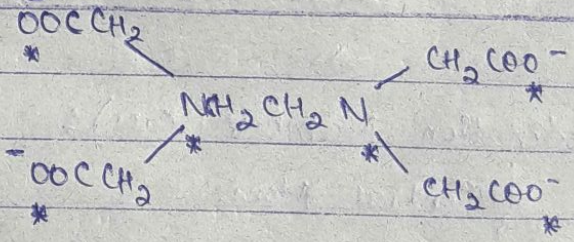


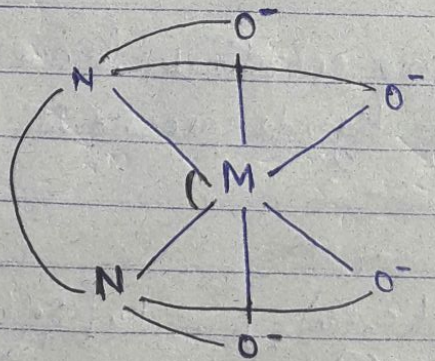
cis-position
(correct)



trans-position
(NOT POSSIBLE!)
(wrong)

→ $[M(EDTA)]^{x-}$





Q

In $[Co(EDTA)]^{3-}$, how many bond angles NCoO are at 90°

Ans : 6

* Ambidentate ligand :
Ligand which can ligate from two different atoms in different complexes.

eg. $M \leftarrow CN^-$ (cyanide)
$M \leftarrow NC^-$ (isocyanide)

$M \leftarrow NO_2^-$ (nitro)
$M \leftarrow ONO^-$ (nitrito)

$M \leftarrow OCN^-$ (cyanate)
$M \leftarrow NCO^-$ (isocyanate)

$M \leftarrow SCN^-$ (thiocyanate)
$M \leftarrow NCS^-$ (isothiocyanate)

→ Coordination Number (C.N) :
of Central Atom.

It is the total no. of sigma coordinate bonds formed by central atom with various ligands around it in complex compound.

eg. $[Ni(CN)_4]^{2-}$ (4), $[Fe(C_2O_4)_3]^{2-}$ (6), $K_4[Fe(CN)_6]$ (6)

$[Ag(NH_3)_2]^+$ (2), $[Pt(en)_3]^{4+}$ (6), $[Co(EDTA)]^-$ (6)

→ Most common C.N are observed to be 6, then 4 and then 2.

⇒ Some common C.N of central atoms –

B, Be → 4

Co^{3+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+} → 6

Ni^{2+} → 4, 6

Pt^{2+} → 4

Pt^{4+} → 6

Ag^{+} → 2

NOTE

- Homoleptic complex:
  Having all ligands same.
  eg. $[Cr(H_2O)_6]Cl_3$

- Heteroleptic complex:
  All ligands are not of same type.

eg. $[Cr(H_2O)_4Cl_2]Cl$

* IUPAC Nomenclature of Coordination Compounds :—

Coordination Sphere
(complex part)

↙ Naming of ligands

↘ Naming of Central atom.

(a) Naming of ligands :

(i) Anionic ligand :

→ A suffix 'o' is applied after removing 'e'.

X^- (halide)	→	halido / halo
Cl^-	→	Chloride / Chloro
I^-	→	Iodido / Iodo
OH^-	→	hydroxido
O^{2-}	→	Oxido / oxo
O_2^{2-}	→	peroxido
O_2^-	→	Superoxido
S^{2-}	→	Sulphido
HS^-	→	Hydrogen Sulphido / mercapto
N^{3-}	→	Nitrido
N_3^-	→	Azido
NH_2^-	→	Amido
NH^{2-}	→	imido
$M \leftarrow CN^-$	→	Cyanido - C
$M \leftarrow NC^-$	→	Cyanido - N
$M \leftarrow NO_2^-$	→	Nitrito - N
$M \leftarrow ONO^-$	→	Nitrito - O
$M \leftarrow OCN^-$	→	Cyanato - O
$M \leftarrow NCO^-$	→	Cyanato - N

gly^- → glycinato
SO_4^{2-} → sulphato
Ox^{2-} → oxalato
$dmgH^-$ → dimethylglyoximato
CH_3COO^- → acetato
H^- → Hydrido.

(ii) Naming of neutral ligands :-

→ Name of neutral ligand remains unchanged except in few cases where special names are used.

imp

CO	– Carbonyl	en	→ ethylene diamine
H_2O	– aqua / aquo	O_2	→ dioxygen
NH_3	– ammine	PH_3	→ Phosphine
NO	– Nitrosyl	CH_3NH_2	→ methyl amine / aminomethane

(iii) Naming of cationic ligand :

→ A suffix 'ium' is applied.
NO^+ → nitrosylium (or) nitrosonium

(b) Naming of Central atom :

→ Name of Central atom remains unchanged if it appears in cationic part or neutral complex.

eg. $[Fe(H_2O)_5(NO^+)]SO_4$
↑ iron

$[Fe(CO_5)]$
↑ iron

→ Name of central atom is modified by applying a suffix 'ate' if central atom appears in anionic ~~part~~ complex part.

eg. $K_4[Fe(CN)_6]$ — anionic complex part; ferrate

Central atom	Name if in Cationic or neutral complex part.	Name if in anionic Complex part
Ti	Titanium	Titanate
Cr	Chromium	Chromate
Mn	Manganese	Manganate
Co	Cobalt	Cobaltate
Zn	Zinc	Zincate
Cu	Copper	Cuperate
Ag	Silver	Argentate
Fe	Iron	Ferrate
Au	Gold	Aurate
Pb	lead	Plumbate
Sn	Tin	Stannate
Hg	Mercury	Mercurate.

(*) Rules of writing IUPAC Name :—

(1) Cationic part is named first followed by anionic part (and a gap in between)

(2) While naming complex part ligands are named first in alphabetical order, No. denoting prefixes are not used in alphabetical order (di, tri, tetra etc)

→ alternate no. denoting prefixes are used (like - bis, tris, tetrakis, pentakis) particularly when ligand is organic or name already contains bi, tri etc.

eg. $(C_2O_4^{2-})_2$ → bis(oxalato)

(3) After naming of all ligands, name of central atom is written along with its oxidation no. in small parenthesis ( ) in roman numerical

eg. Co^{3+} → Cobalt (III) or Cobaltate (III)

(4.) Number denoting prefix is not required to be written if all counter ions are of same type.

eg. $K_4[Fe^{+2}(CN)_6]$ → common Name : Potassium ferrocyanide.

Tetrapotassium Hexacyanido - c ferrate (II) ✗

Potassium Hexacyanido - c ferrate (II) ✓ (IUPAC)

• $K_3[Fe^{+3}(CN)_6]$ → Common Name : Potassium ferricyanide

Potassium hexacyanido - c ferrate (III)

eg. $K_2Na_2[Fe(CN)_6]$

Dipotassium disodium hexacyanido - c ferrate (II)

Imp eg. $Fe_4^{(+3)}[Fe^{(+2)}(CN)_6]_3$ → Prussian Blue

Common Name : ferriferrocyanide

IUPAC name : Iron (III) hexacyanido - c ferrate (II)

→ Turnbull's blue

$Fe_3[Fe(CN)_6]_2$ common name : ferroferricyanide

Iron (II) hexacyanido-c ferrate (III)

Q. Write IUPAC Name—

(i) $[Fe(C_2O_4)_3]^{3-}$ tris(oxalato) ferrate (III) ion

(ii) $[Co(NH_3)_3BrClI]$ ~~triamine~~ triamminebromidochloridoiodidocobalt (III)

(iii) $[PtCl_2(en)_2]$ dichloridobis(ethylenediamine) platinum (II)

(iv) $[Fe(H_2O)_5(NO)]SO_4$ → Brown ring complex Pentaaquanitrosonium iron (I) sulphate

(v) $Na_2[Fe(CN)_5(NO)]$ Sodium pentacyanido-c nitrosonium ferrate (II)

Common name : Sodium Nitroprusside

NOTE : Remember ! # Pakka Se !

In Brown ring complex and sodium nitroprusside, NO^+ is the ligand.

Q. Write IUPAC name,

(i) $[Co(edta)]^-$ ethylenediaminetetraacetatocobaltate (III) ion

(ii) $[Co(NH_3)_6][Co(ONO)_6]$ Hexaammine cobalt (III) hexanitrito-O cobaltate (III)

+1 +1 +5
+2 +4
+3 +3 — Common O.N should be taken if not mentioned.

Imp NOTE

Some common O.N

Sc, Al → +3	Ag → +1, +3
Zn, Cd → +2	Au → +2, +4
Co → +2, +3	Pt → +2, +4
Fe → +2, +3	

Alkali metals → +1 (always)
Alkaline earth metals → +2 (always)

* Naming of Some Special Complexes :

(a) Naming of Bridged complexes :

Bridged complex : which has atleast one bridging ligand.

Bridging ligand: Ligand which is attached to two central atoms.

eg. CO, CN^-, NH_2^-, NH^{2-}, H^-, O^{2-}, O_2^{2-}, O_2^-, Cl etc.

→ A prefix 'μ' is applied before bridging ligand.

eg. $[Co(NH_3)_5 - \underbrace{OH}_{\text{bridging ligand}} - Cr(H_2O)_5]Cl_5$

terminal ligand — bridging ligand — terminal ligand.

μ-hydroxidopentaammminecobalt (III) pentaaqua chromium (III) chloride

OR

Pentaammine cobalt (III)- μ - hydroxidopentaaqua chromium (III) chloride

eg. $\left[Co(en)_2 \begin{matrix} x \\ \end{matrix} \begin{matrix} -1 \\ CN \\ \\ OH \\ -1 \end{matrix} Cr(H_2O)_4 \right]_{y} (SO_4)_2$

$x - 1 - 1 + y - 4 = 0$

$x + y = 6$

$x = 3, \; y = 3$

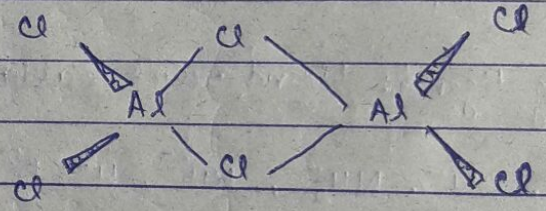
μ-cyanido-μ-hydroxidotetraaquachromium(III) bis(ethylene diamine) cobalt(III) sulphate.

Q Write IUPAC name of

(i) Al_2Cl_6

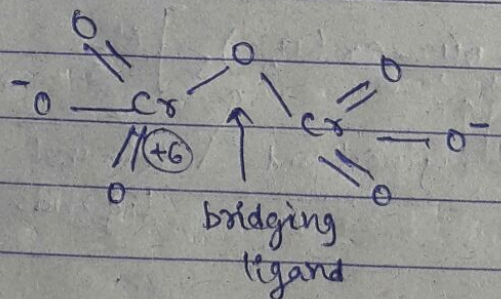
(ii) $Cr_2O_7^{2-}$

Soln (i) Al_2Cl_6



di-μ-chloridobis(dichloridoaluminium(III))

(ii) $Cr_2O_7^{2-}$

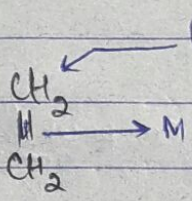


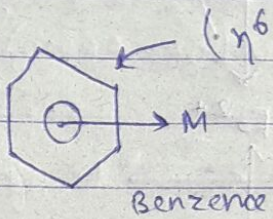
μ-oxidodi(trioxidochromate(VI)) ion.

(b) Naming of π-bonded Complexes

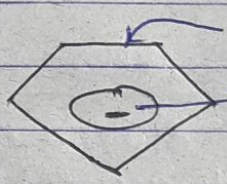
↑ non-classical ligands.

→ In certain complex compound ligand donate π-electron density to the central atom.

eg. 

eg. 

Benzene

eg. 

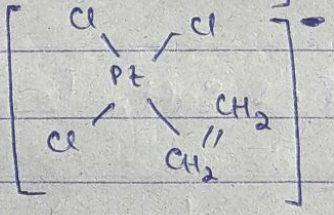
Cyclopentadienyl ion

'eta' → η^x → x represents no. of continuous carbon atoms which are coordinated to central metal atom (also known as Hapticity of Ligand)

eg. Zeise's Salt :

(organometallic compound)

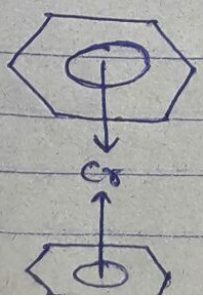
$K[PtCl_3(\eta^2 - C_2H_4)]$ Potassium trichlorido(ethylene) platinate (II) { IUPAC NAME }

or K^+ 

eg. $[Cr(\eta^6 - C_6H_6)_2]$ (organometallic compound)

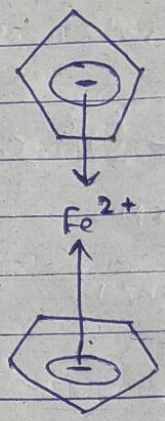
0

Bis(benzene) chromium (0)



eg. Ferrocene, $[Fe(\eta^5 - C_5H_5)_2]^{(+2)}$

bis (cyclopentadienyl) iron (II)



(Sandwiched Structure)

Organometallic compound.

* Organometallic Compounds:

Compounds in which carbon of organic group is directly attached to a metal / metalloid / non-metal

except (1) Noble Gases
(2) Halogens
(3) Chalcogens
(4) N & P

eg. of organometallic compounds —

→ $Cr(\eta^6 - C_6H_6)_2$, Zeise's Salt, Ferrocene

→ $(C_2H_5)_2Zn$, $(C_2H_5)_4Pb$, $(C_2H_5)_4Sn$, $(C_2H_5)_3B$

↑ Tetraethyl lead (TEL) used as antiknocking substance in gasoline.

→ Grignard reagent, RMgI
eg CH_3MgI

→ RLi etc.

→ Carbonyl compounds
eg. $[Fe(CO)_5]$, $[Ni(CO)_4]$

→ Cyanido Compounds
$K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$

Q. which is/are not organometallic compound ?

A. $(C_2H_5)_4Sn$

B. $CH_3\bar{O}Na^+$

C. $CH_3\dot{C}OOK^+$

D. C_2H_5MgBr

Ligands

Classical

Non-Classical ligands

(a) Classical ligands :

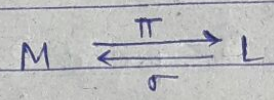
Classical ligand, which donate L.P of e^- to the central atom and do not any back bonding due to the absence of vacant 'd' orbital or π^* MO π ABMO in valence shell.

M ⟵ :L
σ-bond

eg. of classical ligands :
H_2O, NH_3, OH^-, NH_2^-, F^- etc.

(b) Non-classical ligands :-
(Also known as π-acid ligand or π-acceptor ligand)

→ These ligand donate either L.P or π-electron density to the central atom and simultaneously for π-back bond from fully filled d-orbital of central atom into vacant 'd' or π* MO (or ABMO) of ligand.



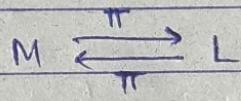
eg. CN^-, CO, N_2

π ABMO is present to accept L.P of central atom.

eg. PH_3, PR_3, PPh_3, PF_3, $P(OR)_3$

Vacant 'd' orbitals are present to accept L.P from central atom

→ act as lewis acid.



eg. C_2H_4, C_2H_2, ,

Vacant π* MO (or ★ ABMO are present to accept L.P of central atom.

→ These ligands are called lewis Base.

→ These non-classical ligand result into synergic bonding
(Refer to synergic bond in carbonyl compound)

* Various Bonding Theories of Coordination Compounds :

(1) Werner's theory
(2) Sidwick's EAN rule
(3) Valence Bond theory (VBT)
(4) Crystal Field theory (CFT)
(5) Ligand field theory (MOT) } NOT in IIT Syllabus

1. Werner's Coordination theory :

Postulates :

(i) Central metal atom satisfies two type of valencies -

→ Primary valency (now known as O.N) which is satisfied by anionic species.

→ Secondary valency (now known as C.N) satisfied by anionic and neutral species.

(ii) Primary valency is ionisable (ionic interaction) and non-directional

→ Secondary valency is ~~non-directional~~ non-ionisable and direction.

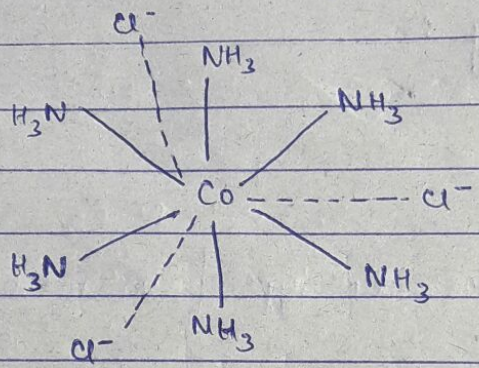
(iii) Geometry of compound is dependent on secondary valencies. For pictorial representation of coordination compound, primary valency is shown by dashed lines (- - - - - -), secondary by solid lines (—).

Some species show both primary and secondary valencies, and are shown by (——)

* Species used in O.N calculation → Primary
Species used in C.N calculation → Secondary
Species used in O.N as well as C.N calculation → primary & Secondary

eg. $[Co^{(+3)}(NH_3)_6]Cl_3$

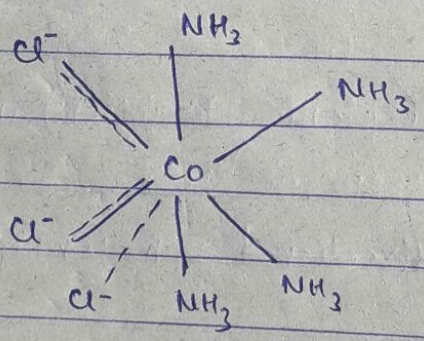
↑ $6NH_3$ Secondary valencies
$3Cl^-$ → Primary



Werner's representation of $CoCl_3 \cdot 6NH_3$ or $[Co(NH_3)_6]Cl_3$

eg. $[Co^{(+3)}(NH_3)_4Cl_2]Cl$ ← Primary

↑ Secondary ↑ $2Cl^-$ serve as primary and secondary both



eg. $CoCl_3 + NH_3(aq)$

1 : 6 (molar) → $CoCl_3 \cdot 6NH_3$
1 : 5 (molar) → $CoCl_3 \cdot 5NH_3$
1 : 4 (molar) → $CoCl_3 \cdot 4NH_3$ } isomers (different)

→ Werner conducted experiments and measured many properties to establish the primary and secondary valencies.

(a) Measurement of Colligative properties :-

↳ lowering in V.P
↳ Elevation in B.P
↳ Depression in F.P
↳ Osmotic pressure

eg. 1 mol of $CoCl_3 \cdot 6NH_3$ in aq. soln

↳ measurement of C.P suggests that solution contains 4 mol of solute particles.

$$\Downarrow$$

$$[Co(NH_3)_6]Cl_3$$

1 mol

$$\downarrow \text{aq. soln}$$

$$\underbrace{[Co(NH_3)_6]^{3+} + 3Cl^-}_{\text{4 mol of particles.}}$$

eg. 1 mol of $CoCl_3 \cdot 4NH_3$ in aq. soln

↳ C.P measurement tells that 2 mol of particles are present.

$$\Downarrow$$

$$[Co(NH_3)_4Cl_2]Cl$$

1 mol

$$\downarrow$$

$$\underbrace{[Co(NH_3)_4Cl_2]^+_{(aq)} + Cl^-_{(aq)}}_{\text{2 mol of particles.}}$$

NOTE Remember that, usually neutral ligands serve as secondary valency.
Except H_2O which can ~~act as prim~~ be outside the coordination sphere.
(Through H-bonding)

(ii) Using Some Chemical reaction :-

eg. 1 mol of $CoCl_3 \cdot 5NH_3(s)$ + $AgNO_3(aq)$ (excess)

→ 2 mol of white ppt is formed which dissolves in aq. NH_3.

$[Co(NH_3)_5Cl]Cl_2$

↓ Ag^+ (excess)

$AgCl\downarrow \xrightarrow{aq.\ NH_3} [Ag(NH_3)_2]^+ + Cl^-$

eg. $\underbrace{CoCl_3 \cdot 4NH_3}_{1\ mol}$ $\xrightarrow[(excess)]{AgNO_3(aq)}$ 1 mol of $AgCl\downarrow$

⇓

$[Co(NH_3)_4Cl_2]Cl$

↳ Ag^+ (excess)

$AgCl\downarrow$ (1 mol)

V. Imp	aq. dil NH_3	aq. conc. NH_3	aq. KCN	aq. $Na_2S_2O_3$ (Hypo)
AgCl ↓ (white)	✓	✓	✓	✓
AgBr ↓ Pale Yellow	✗	✓	✓	✓
AgI ↓ Bright yellow	✗	✗	✓	✓

↳ Dissolution of AgX (ppt) in Solution.

$$AgCl_{(s)} + aq.\ NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]\ Cl_{(aq)}$$

$$AgBr_{(s)} + aq.\ KCN \longrightarrow [Ag(CN)_2]^-_{(aq)}$$

$$AgI_{(s)} + aq.\ hypo \longrightarrow [Ag(S_2O_3)_2]^{3-}_{(aq)}$$

eg. dehydrating substance, conc. H_2SO_4 attacks water of crystallization but not the H_2O ligand.

$$[M(H_2O)_y]^{x+}\ Cl_x \cdot \underbrace{zH_2O}_{\text{water of crystallization}} \xrightarrow[H_2SO_4]{\text{conc.}} \text{mass gain of conc. } H_2SO_4 \text{ is '18z' g.}$$

($[M(H_2O)_y]$: ligand)

eg. $CrCl_3 \cdot 6H_2O \xrightarrow[H_2SO_4]{\text{conc.}}$ mass gain of H_2SO_4 is zero gram (or No mass gain)

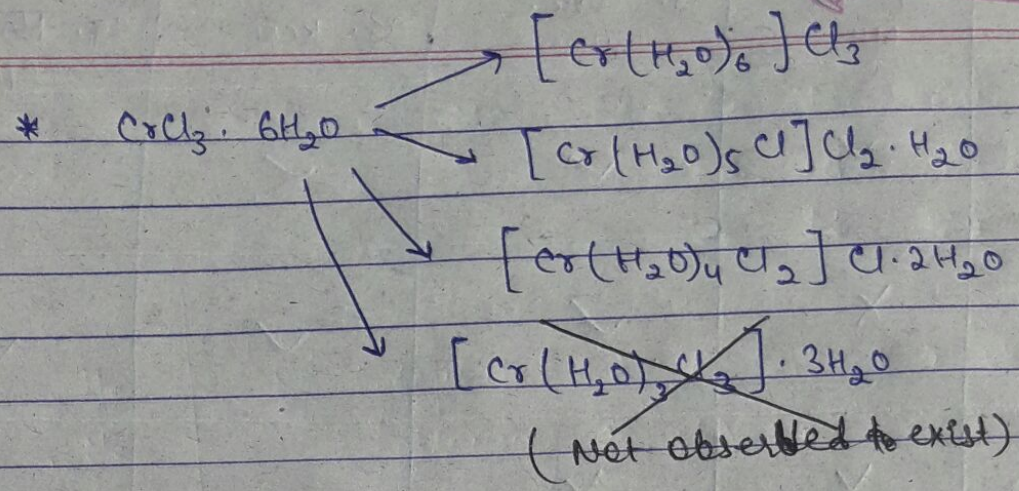
1 mol

$\Downarrow$

$(Cr(H_2O)_6)Cl_3$

eg. $CrCl_3 \cdot 6H_2O \xrightarrow[H_2SO_4]{\text{conc.}}$ 36g mass gain by H_2SO_4

1 mol $\Downarrow$ $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$



(iii) By measurement of Electrical Conductance :

→ Electrical conductance of an electrolyte is dependent on no. of charged particles per formula unit and charge on ions.

Charge ↑ , E.C ↑ || No. of ions ↑ , E.C ↑

eg. 1 mol of $CoCl_3 \cdot 6NH_3$ in aq. medium shows electrical conductance corresponding to 4 mol of charge particles and 6 units of electrical charge

$$[Co(NH_3)_6]Cl_3$$

$$[Co(NH_3)_6]^{3+}_{(aq)} + 3Cl^-_{(aq)}$$

4 mol of particles , 6 unit of electrical charge

Q Match the column :

Compound (1 mol)	Conductance
$[Ni(CO)_4]$	0
$K_4[Fe(CN)_6]$	5
KCl	2
$BaCl_2$	3

2. Sidwick's EAN rule : ($18e^-$ rule i.e 18 e^- in valence shell)

↑ Effective atomic Number of Central atom.

EAN of central atom

= Atomic No. of central − O.N of central atom + total no. of e^- obtained from various ligands

→ According to this rule, if central atom in a complex has EAN = atomic number of a nearby noble gas, then complex is stable. Otherwise unstable.

→ This is now not valid as most complexes which are stable do not follow this rule.

V. Imp → This Rule is still well applicable for carbonyl compounds. (or metal carbonyls)

	$_{21}Sc$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	$_{30}Zn$
						Rh	Pd	Ag	$_{48}Cd$	
						Ir	Pt	Au	$_{80}Hg$	

$_{2}He$	
$_{10}Ne$	
$_{18}Ar$	
$_{36}Kr$	
$_{54}Xe$	
$_{86}Rn$	

Q Calculate EAN of central atom in following complexes -

(i) $[Ag(NH_3)_2]Cl$ (ii) $[RhCl(PPh_3)_3]$

(iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[Fe(CO)_5]$

(v) $[Co(NH_3)_4Cl_2]Cl$ (vi) $K_4[Fe(CN)_6]$

(vii) $K_3[Fe(CN)_6]$ (viii) $[AuCl_4]^-$

(i) $47-1+4=50$ (does not follow EAN)

(ii) $45-1+8=52$ ✗

(iii) $26-3+12=35$ ✗

(iv) $26-0+10=36$ ✓

(v) $27-3+12=36$ ✓

(vi) $26-2+12=36$ ✓

(vii) $26-3+12=35$ ✗

(viii) $79-3+8=84$ ✗

NOTE (1) All π-electrons should be counted in calculation of EAN in π-bonded complexes.

eg. $[Cr(\eta^6 - C_6H_6)_2]$

EAN = 24 − 0 + 2×6 = 36 (yes, it follows EAN rule)

6e⁻ donor

eg. ferrocene, $[\overset{+2}{Fe}(\eta^5 - C_5H_5)_2]$

EAN = 26 − 2 + 2×6
= 36 (follows EAN)

Imp (2) Nitrosyl group (NO) is a 3e⁻ donor which is evident from the following reactions.

eg. $[Cr(CO)_6] + 4NO \longrightarrow [Cr(NO_4)] + 6CO$

(NO ligand is 3e⁻ donor)

EAN = 24 − 0 + 6×2
= 36 (follows EAN)

EAN = 24 − 0 + 4×3
= 36 (follows EAN)

eg. $[Fe(CO)_5] + 2NO \longrightarrow [Fe(CO)_2(NO)_2] + 3CO$

EAN = 26 − 0 + 10
= 36

EAN = 26 − 0 + 2×2 + 2×3
= 36

* NO^+ is a normal 2e⁻ donar.

(3) EAN rule applies very well on carbonyl compounds (with a notable exception of $V(CO)_6$).

eg. $[Cr(CO)_6]$, EAN = 24 − 0 + 12 = 36

$[Fe(CO)_5]$, EAN = 26 − 0 + 10 = 36

$[Ni(CO)_4]$ EAN = 28 − 0 + 8 = 36

} All follow EAN

eg. $Mn(CO)_5$ (monomeric form)

↑

EAN = 25 − 0 + 10 = 35 (does not follow EAN rule) and hence does not exist. ~~monomer~~

It exists in either dimeric form or gets reduced easily into anionic form and follows EAN rule

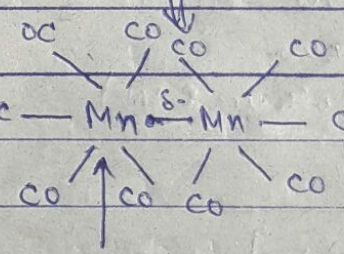
reduced in presence of R.A → $[Mn(CO)_5]^-$

↑

EAN = 25 − (−1) + 10

= 36 (follows EAN)

dimerised → $[Mn_2(CO)_{10}]$



EAN = 25 − 0 + 2 × 5 + 1

= 36 (follow EAN)

eg. $[Co(CO)_4]$

↑

EAN = 27 − 0 + 4 × 2 = 35 (does not follow EAN and monomer does not exist)

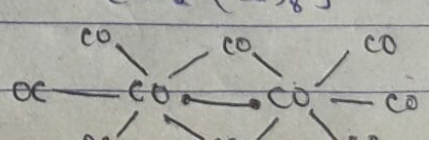
either forms anion → $[Co(CO)_4]^-$

↑

EAN = 27 − (−1) + 4 × 2

= 36

or forms dimer → $[Co_2(CO)_8]$

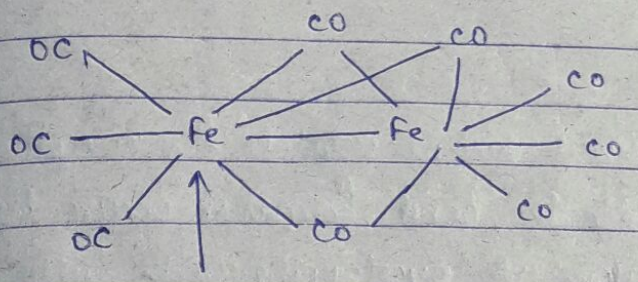


EAN = 27 − 0 + 3 × 2 + 2

= 36

eg. Polymeric Carbonyl of fe.

$Fe_2(CO)_9$



EAN = 26 - 0 + 6 + 3 + 1

= 36 (follow EAN)

Q. Find x if $H_x[CO(CO)_4]$ complex exists.

$-x \leftarrow$ O.N of CO

Sol" CO must follow EAN rule

EAN = 36 = 27 - (-x) + 8

x = 1 Ans.

Imp NOTE $[V(CO)_6]$ → exists and does not follow EAN rule.

(a paramagnetic octahedral complex)

EAN = 23 - 0 + 12 = 35 (does not follow EAN, yet exists)

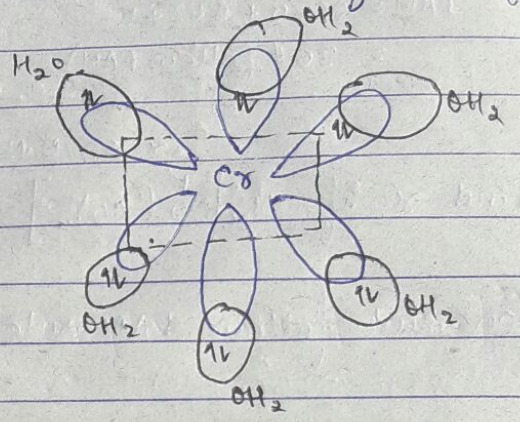
[Exception of EAN Rule]

* Valence Bond theory (VBT)

Postulates :

→ Central atom provides hybridized vacant orbitals for accepting L.P from various ligands. Coordinate bond formation occurs between vacant orbital of central atom via overlapping with fully filled orbitals of ligands.

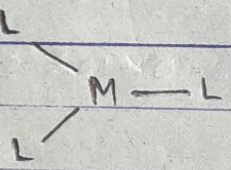
eg. $[Cr(H_2O)_6]^{3+}$



→ No. of vacant hybrid orbitals of central atom depends on Coordination Number.

CN = 2 , Sp , Linear L — M — L

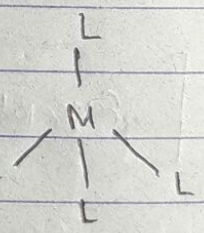
CN = 3 , Sp^2 , Trigonal planar,

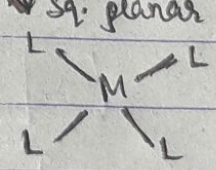


CN = 4 → Sp^3 $(ns + np^3)$, Tetrahedral ,

→ dsp^2 $((n-1)d_{x^2-y^2} + ns + npx + npy)$

→ d^3s (Tetrahedral)





$(n-1)d_{xy} + (n-1)d_{yz} + (n-1)d_{zx} + ns$

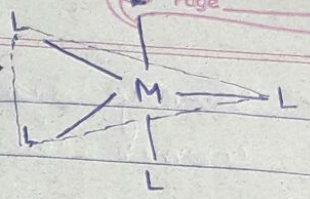
usually found for d^0 configuration of d-block metals.

(VO_4^{3-}, CrO_4^{2-}, MnO_4^-, MnO_4^{2-}, $TiCl_4$)

$Cr_2O_7^{2-}$

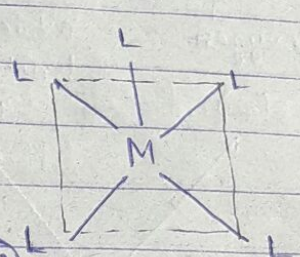
CN = 5 → dsp^3 | sp^3d , Trigonal Bipyramidal

dsp^3: $(n-1)d_{z^2} + ns + np^3$; sp^3d: $ns + np^3 + nd_{z^2}$



dsp^3 | sp^3d , Square pyramidal

$(n-1)d_{x^2-y^2} + ns + np^3$; $ns + np^3 + nd_{x^2-y^2}$



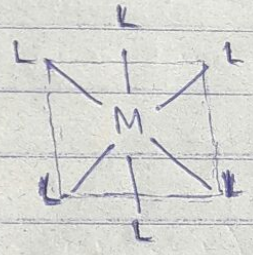
• eg. $[Ni(CN)_5]^{3-}$ (+2)

Due to pseudoberry rotation, it converts into TBP also but its major constituent is Sq. pyramidal

(fluxonal species like NH_3, PF_5)

CN = 6, d^2sp^3 | sp^3d^2 , Octahedral

$(n-1)d_{z^2} + (n-1)d_{x^2-y^2}$; $ns + np^3 + nd_{z^2} + nd_{x^2-y^2}$



→ In case of CN = 2, 3, no additional information is needed to predict shape / hybridisation of complex compound. But in CN = 4, 5, 6, some extra experimental info (eg. no. of unpaired e^- etc) is needed to predict shape / hybd^n.

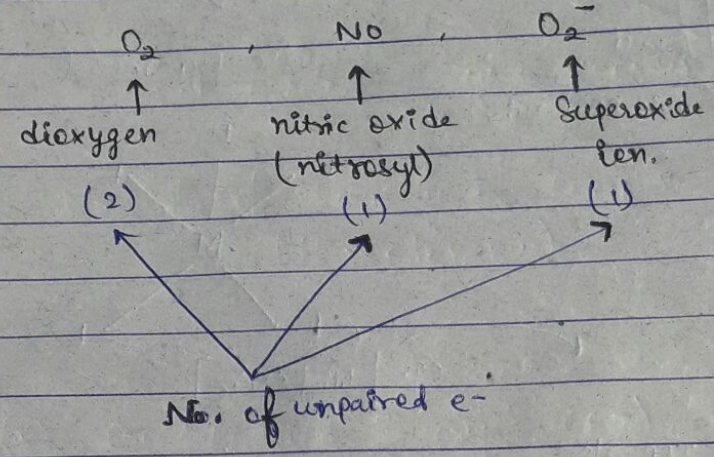
(Infact this is a drawback of VBT)

No. of unpaired e^- in complex part

= No. of unpaired e^- in central atom

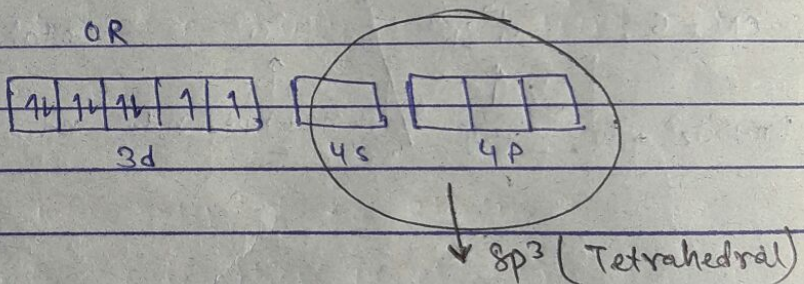
+ No. of unpaired e^- in ligands.

* Usually ligands are diamagnetic except the following common cases :



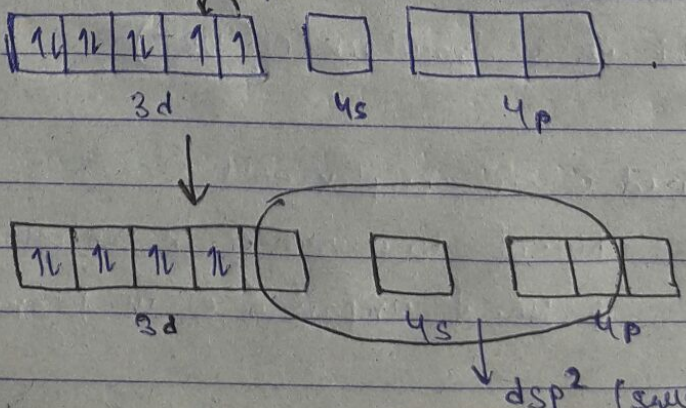
Q. eg. Find shape / hybd^n of complex anion $[NiCl_4]^{2-}$ having 2 unpaired e⁻

Soln Ni^{2+} : $[Ar]\ 3d^8\ 4s^0\ 4p^0\ 4d^0$



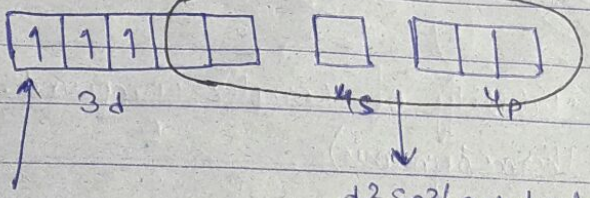
Q. Find shape / hybd^n of a diamagnetic complex anion. $[Ni(CN)_4]^{2-}$ (+2)

Soln : $Ni^{2+} = 3d^8\ 4s^0\ 4p^0$



Q. Find Spin magnetic moment, hybdⁿ & shape of $[Cr(H_2O)_6]^{3+}$ (+3)

Soln: Cr^{3+} : $3d^3$ $4s^0$ $4p^0$



d^2sp^3 (octahedral)

x = 3 unpaired e^-

Spin magnetic moment = $\sqrt{x(x+2)}$ B.M

= $\sqrt{15}$ B.M

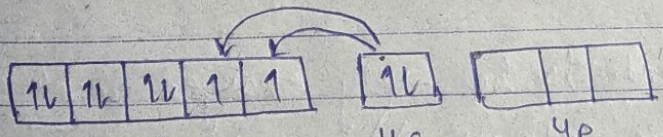
Q. Find spin magnetic moment, hybdⁿ and ~~sp~~ shape of monomeric nickel carbonyl.

Soln $[Ni(CO)_x]$ EAN = 36 = 28 − 0 + 2x

x = 4

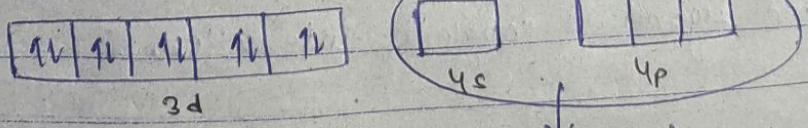
$[Ni(CO)_4]$ (0)

Ni : [Ar] $3d^8$ $4s^2$ $4p^0$ $4d^0$



Possibilities in CN = 4

sp^3 or dsp^2



sp^3 (tetrahedral)

No unpaired e^- i.e spin magnetic moment = 0

* Drawbacks of VBT :

(1) No info of magnetic nature

(2) Does not predict colours of coordination compounds.

(3) No info of stability of complex compound. (thermodynamic)

(*) Crystal Field Theory (CFT)

Postulates :

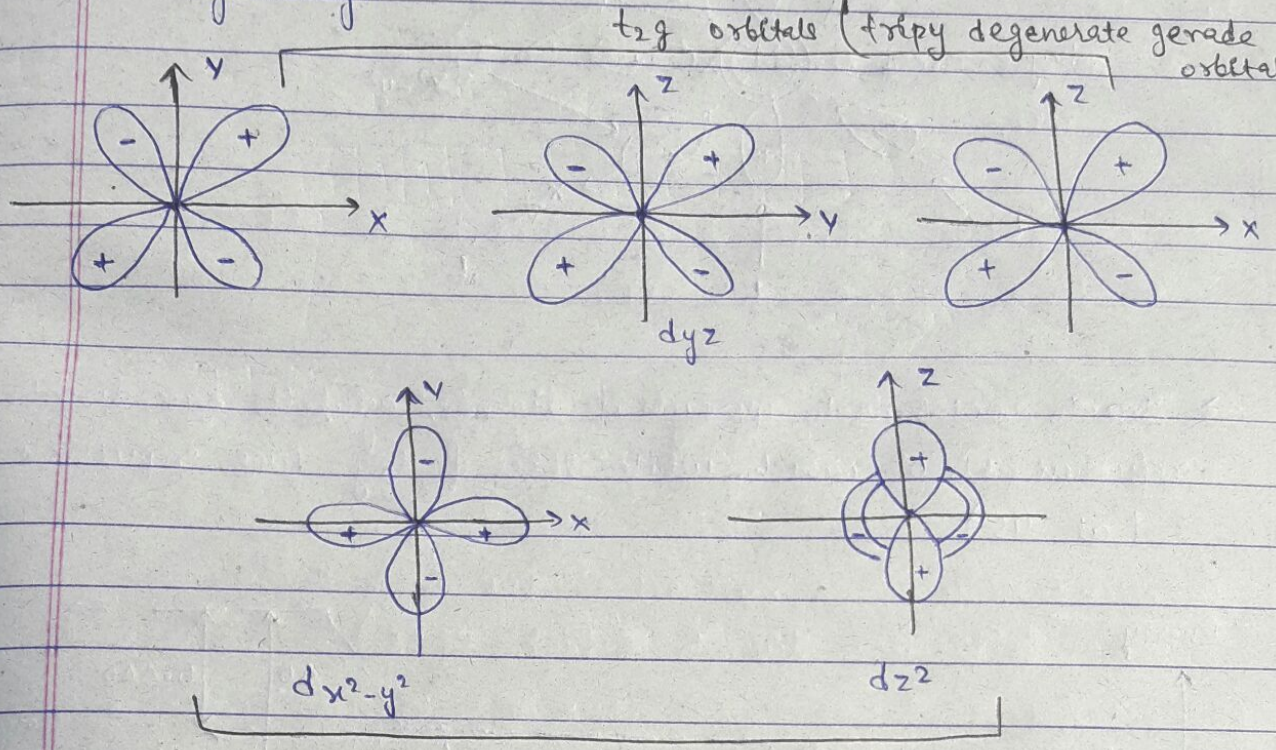
→ Originally this theory was applied in physics to study the repulsions faced by cations due to approaching anions considering anions to be negatively charged point charges. (Ionic interaction)

→ later this theory was extended for ~~studs~~ coordination compounds to study modification in electronic configuration of central atom due to approach of ligands.

(considering ligands to be -vely charged point charges (assumed ionic interaction))

imp (Infact this is drawback of CFT on coordination compound because the actual interaction between central atom and ligand is covalent interaction.

→ Energy of d-orbitals of central atom gets modified due to approach of ligands and these five 'd' orbitals lose their degeneracy.



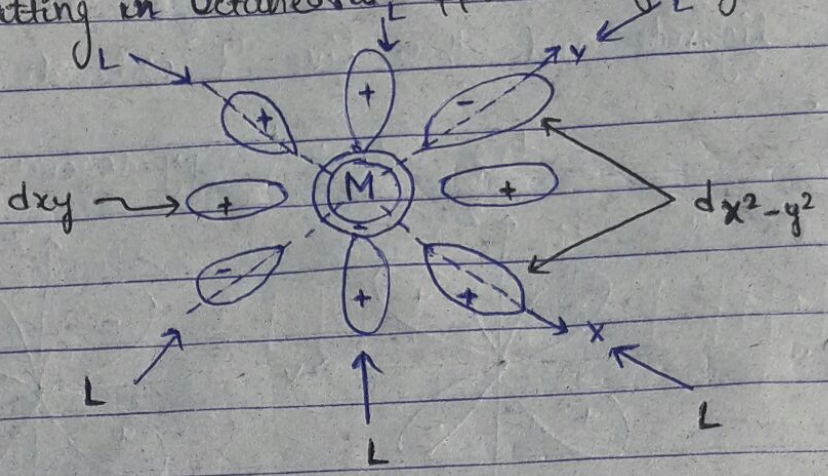
→ Orientation of various d-orbitals of central atom can be imagined in an imaginary cube.

⇒ Taking central atom to be located at body centre of cube,

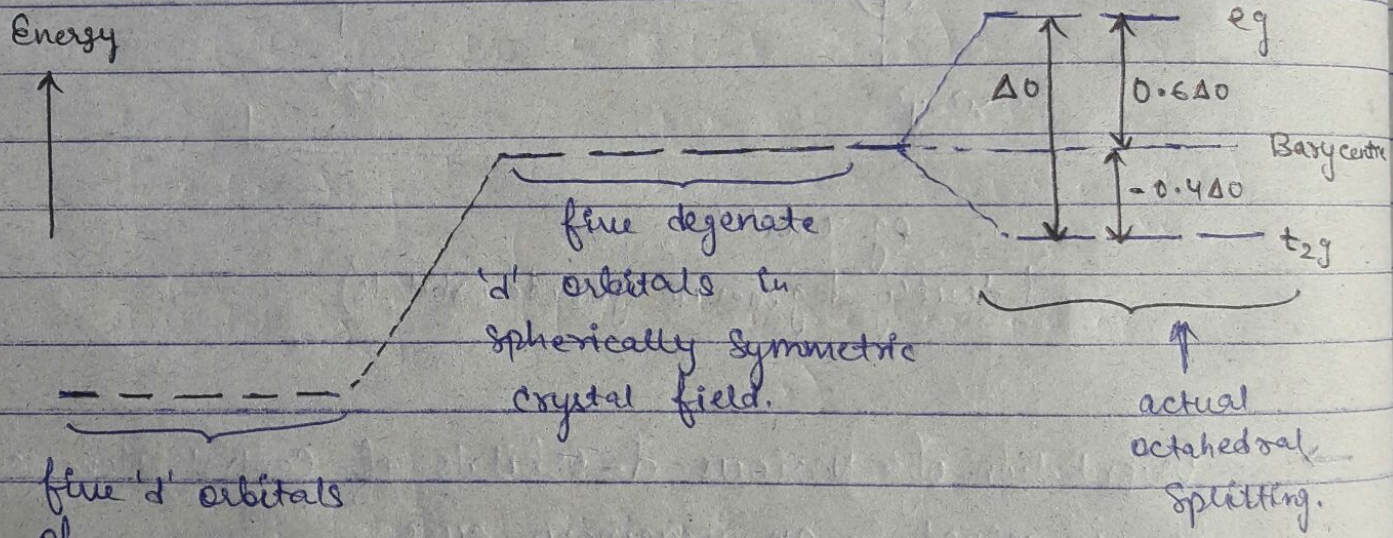
⇒ 12 lobes of t_{2g} are pointing towards the 12 edge centres of cube.

⇒ 6 lobes of e_g are pointing towards 6 face centres of cube while the ring of dz^2 is in xy plane.

* Splitting in octahedral approach of ligands :-



→ Due to octahedral approach of ligands, eg lobes face direct repulsion at 0° ~~which~~ while lobes of t_{2g} face repulsion (at 45°).



$\Delta 0$ = Octahedral Splitting energy = $\frac{hc}{\lambda}$

= Energy diff. between eg and t_{2g} orbitals.

→ under approach of 6 ligands, e^- of central atom get redistributed depending upon energy of t_{2g} and e_g

→ first $3e^-$ are filled in t_{2g} orbitals (one each)

→ 4^{th} e^- may pair up in t_{2g} or may jump to e_g depending up of relative values of Δ_o and pairing energy (P)

If $\Delta_o > P$, 4^{th} e^- pairs up in t_{2g}
If $\Delta_o < P$, 4^{th} e^- will jump into e_g.

→ Taking 'P' is not much variable, (Take constant)
4^{th} e^- mainly depends on Δ_o.

* Factors affecting Δo :

(1) Nature of ligand :
Some ligands which cause very high splitting ($> P$) are called strong field ligands (SFL)
Some ligands cause less splitting ($\Delta_o < P$), are called weak field ligands (WFL)

→ Strength of various ligands are experimentally measured and the order (increasing) is arranged in a series called Spectrochemical Series.

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NCH_3 < Py < NH_3 < en < bipy < NO_2^- < CN^- < CO$$

Increasing order of strength of ligands.

* Upto H_2O, ligands are (in general) are considered to be WFL.

* ligands with donor X (F, Cl, Br, I), O, S are generally WFL.

* Beyond H_2O, ligands are considered to be SFL
  * donor N, P, C are SFL.

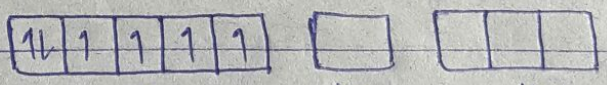
* CN^-, CO are very strong field ligands due to synergic bond. (π-back)

Exception: H_2O and ox^{2-} act as SFL with Co^{2+}
(This is due to high CFSE)

$[Co(H_2O)_6]^{3+}$ } Both are d^2sp^3 (inner orbital complexes)

$[Co(C_2O_4)_3]^{3-}$ } (Also they are low spin or spin paired complex)

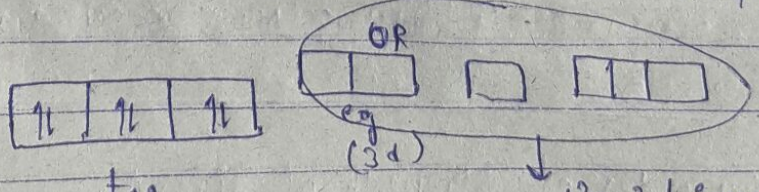
Co^{3+} : [Ar] $3d^6\ 4s^0\ 4p^0$



⇒ with Co^{3+}, H_2O / ox^{2-} act as SFL

⇓

$t_{2g}^{2,2,2}$, $eg^{0,0}$ (under the influence of H_2O / ox^{2-} as SFL)



d^2sp^3 (Inner orbital complex)

(2) Z_{eff} of central atom / Type of central metal atom :

$3d < 4d < 5d$

increasing Z_{eff}

$\therefore$ Increase Δ_o

→ With 4d or 5d metal, almost every ligand act as SFL due to high Δ_o caused.

(3) Oxidation Number of central atom :

→ Higher is the +ve O.N of metal, greater will be Z_{eff}. and hence greater will be Δ_o

$Co^{3+} > Co^{2+}$

$Ni^{4+} > Ni^{2+}$

$Fe^{3+} > Fe^{2+}$

greater Z_{eff}.

* Higher O.N of metal favours pairing of e^- (if possible) and hence favour formation of low spin complex

eg. $[\overset{(+2)}{Ni}F_6]^{4-}$ → sp^3d^2 (outer orbital complex)

$[\overset{(+4)}{Ni}F_6]^{2-}$

↘ d^2sp^3 (low spin complex) / Inner orbital complex. due to high O.N of Ni. or F^- acts as SFL with Ni^{4+}

↙ will take it in exception.

Notable Exceptions : (Imp)

(1) $[Ni(CN)_6]^{4-} \rightsquigarrow d^2sp^3$ (low spin or spin paired complex)

(2) with Co^{3+}, ligands like H_2O, Ox^{2-} act as SFL.

V. Imp
IIT

$[Co(H_2O)_6]^{3+}$
$[Co(ox)_3]^{3-}$
} d^2sp^3 (low spin complex)

Note: $[Co(H_2O)_3F_3] \cdot [CoF_6]^{3-}$

sp^3d^2 (outer orbital complex)

(3) with Mn^{2+}, Fe^{2+}, Co^{2+}, NH_3 acts as WFL and forms outer orbital complex.

$[Mn(NH_3)_6]^{2+}$
$[Fe(NH_3)_6]^{2+}$
$[Co(NH_3)_6]^{2+}$
} $\rightarrow sp^3d^2$ outer orbital complex (or high spin or spin free complexes)

(*) Crystal field stabilization energy (CFSE)

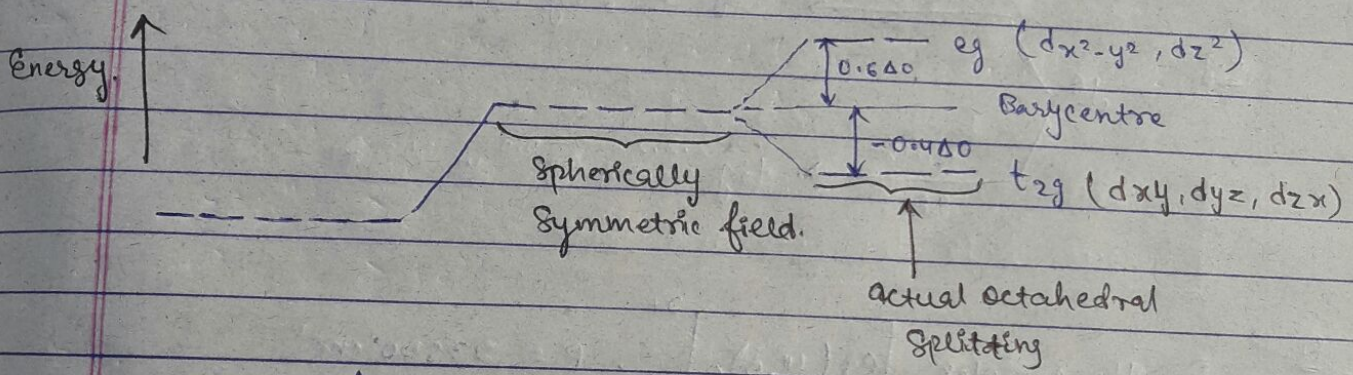
It is the enthalpy change (or energy released) in presence of actual ligand field. (Octahedral / Sq. planar / tetrahedral etc) relative to spherically symmetric crystal field.

→ CFSE is either -ve or zero (not +ve)

→ Higher CFSE released contributes in higher stability of complex.

* CFSE is not the only factor which decides stability of complex. Infact strength of bond formed between central atom and ligand is most contributing factor for stability of complex.

→ eg. 'd' conf^n (eg. $[\overset{+3}{Ti}(H_2O)_6]^{3+}$



CFSE for $[Ti(H_2O)_6]^{3+} = -0.4\Delta_o$

e.g d^2 conf^n. (CN = 6), $t_{2g}^{1,1,0}$, $eg^{0,0}$

$$CFSE = -0.4\Delta_o \times 2$$
$$= -0.8\Delta_o$$

* General expression of CFSE for octahedral complex:

$$CFSE = -0.4\Delta O \times n_{t_{2g}} + 0.6\Delta_o \times n_{eg} + x \times p$$

where Δ_o = octahedral splitting energy

P = pairing energy

n_{t_2g} = no. of e^- filled in t_2g orbitals

n_{eg} = no. of e^- filled in eg orbitals

x = No. of extra pairs formed in actual ligand field relative to spherically symmetric field.

e.g

d^4 → with WFL → $t_2g^{1,1,1}$, $eg^{1,0}$, $x = 0$

d^4 → with SFL → $t_2g^{2,1,1}$, $eg^{0,0}$, $x = 1$

e.g

d^6 → with WFL → $t_2g^{2,1,1}$, $eg^{1,1}$, $x = 0$

d^6 → with SFL → $t_2g^{2,2,2}$, $eg^{0,0}$, $x = 2$

Q. For the complex $[Cr(H_2O)_6]^{2+}$, $P = 23500\ cm^{-1}$, $\Delta_o = 12600\ cm^{-1}$. Find state of hybd^n of Cr atom in complex and CFSE.

Sol^n: Since, $\Delta_o < P$, H_2O → WFL

sp^3d^2 ^4Ag. , Cr^{2+} : $3d^4$

$t_2g^{1,1,1}$, $eg^{1,0}$

$CFSE = -0.4\Delta_o \times 3 + 0.6 \times \Delta_o \times 1 + 0$

$= -0.6\Delta o$

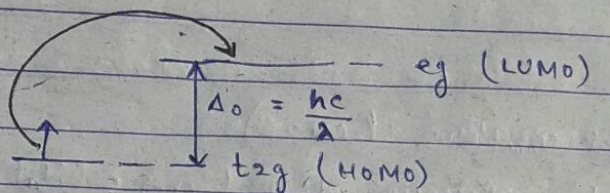
$= -0.6 \times \frac{hc}{\lambda} = -0.6 \times hc\bar{v}$ ← wave no.

$= -0.6 \times 6.62 \times 10^{-34} \times 3 \times 10^8 \times 12600 \times 10^2$ Joule

* → Δ_o is more accurately measured with d^1 confⁿ.

eg $[Ti(H_2O)_6]^{3+}$, $Ti^{3+}: 3d^1$

$t_{2g}^{1,0,0}$, $eg^{0,0}$



E.C, d^x	Examples	Ligand	t_{2g} , eg	CFSE	Hybdⁿ.
d^0	Sc^{3+}, Ti^{4+}	—	$t_{2g}^{0,0,0}$, $eg^{0,0}$	zero	d^2sp^3
d^1	Ti^{3+}, V^{4+}	—	$t_{2g}^{1,0,0}$, $eg^{0,0}$	$-0.4\Delta_o$	d^2sp^3
d^2	Ti^{2+}, V^{3+}	—	$t_{2g}^{1,1,0}$, $eg^{0,0}$	$-0.8\Delta_o$	d^2sp^3
d^3	V^{2+}, Cr^{3+}	—	$t_{2g}^{1,1,1}$, $eg^{0,0}$	$-1.2\Delta_o$	d^2sp^3
d^4	Cr^{3+}, Mn^{3+}	WFL	$t_{2g}^{1,1,1}$, $eg^{1,0}$	$-0.6\Delta_o$	sp^3d^2
		SFL	$t_{2g}^{2,1,1}$, $eg^{0,0}$	$-1.6\Delta_o + 1P$	d^2sp^3
d^5	Mn^{2+}, Fe^{3+}	WFL	$t_{2g}^{1,1,1}$, $eg^{1,1}$	zero	sp^3d^2
		SFL	$t_{2g}^{2,2,1}$, $eg^{0,0}$	$-2.0\Delta_o + 2P$	d^2sp^3
d^6	Fe^{2+}, Co^{3+}	WFL	$t_{2g}^{2,1,1}$, $eg^{1,1}$	$-0.4\Delta_o$	sp^3d^2
		SFL	$t_{2g}^{2,2,2}$, $eg^{0,0}$	$-2.4\Delta_o + 2P$	d^2sp^3
d^7	Co^{2+}	WFL	$t_{2g}^{2,2,1}$, $eg^{1,1}$	$-0.8\Delta_o$	sp^3d^2
		SFL	$t_{2g}^{2,2,2}$, $eg^{1,0}$	$-1.8\Delta_o + P$	d^2sp^3

this e⁻ will be transferred or migrated by a very strong field ligand.

d^8	Ni^{2+}	—	$t_{2g}^{2,2,2}, eg^{1,1}$	$-1.2\Delta_o$	sp^3d^2
d^9	Cu^{2+}	—	$t_{2g}^{2,2,2} eg^{2,1}$	$-0.6\Delta_o$	sp^3d^2
d^{10}	Cu^+, Zn^{2+}	—	$t_{2g}^{2,22}, eg^{2,2}$	zero	sp^3d^2

V. imp **Note:**

(i) In octahedral complexes (CN = 6)

d^0 to d^3, always d^2sp^3 (inner orbital complex)

d^8 to d^{10}, always sp^3d^2 (outer orbital complex)

→ d^4 to d^7, complex may be d^2sp^3 or sp^3d^2 depending upon nature of ligand

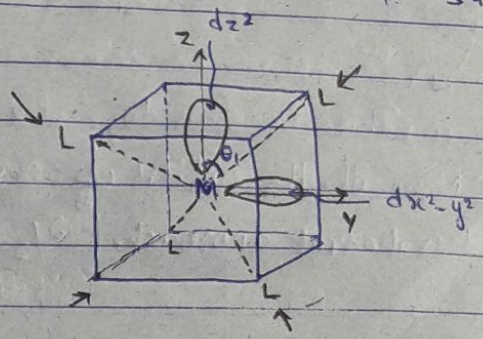
Also the term, low spin (or spin paired) and high spin (or spin free) are defined only for d^4 to d^7 confⁿ. because both low spin and high spin possibilities are there.

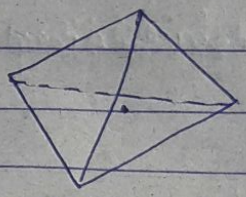
* Splitting in CN = 4

$\theta_1 = \frac{109°28'}{2}$

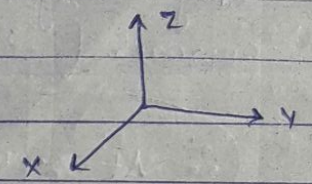
$\theta_1 = 54°44'$

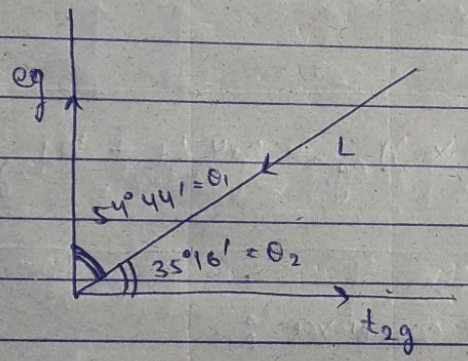
(a) Tetrahedral splitting :



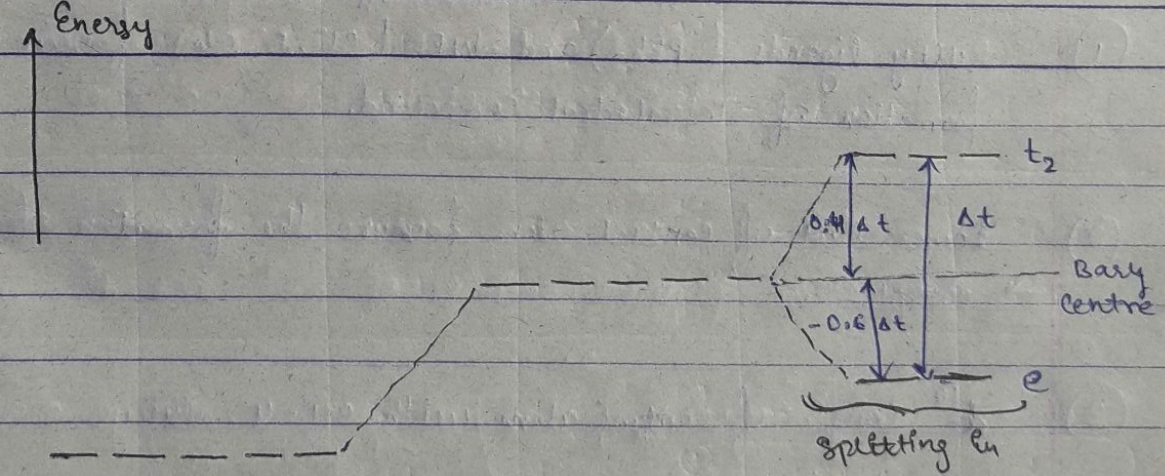


4 equilateral triangles in regular tetrahedron.





→ Repulsions faced by t_{2g} orbitals is greater (at 35°16') than that in eg orbitals (at 54°44')



splitting in tetrahedral approach.

* Tetrahedral geometry lacks centre of inversion (i.e no more gerade orbitals)

→ $\Delta t \approx \frac{4}{9} \times \Delta_o$ [This shows tetrahedral splitting energy is much smaller than that in octahedral splitting.]

This is due to

(i) None of the orbital of central atom faces direct repulsion in tetrahedral approach. (2/3 factor)

(ii) Only 4 ligands approach against 6 in octahedral approach (2/3 factor)

$\therefore \Delta t \approx \frac{4}{9} \Delta_o$ Remember!

$$(CFSE)_{\text{Tetrahedral}} = -0.6\,\Delta t \times n_{eg} + 0.4\,\Delta t + n_{t_{2g}}$$

V.Imp

Guidelines to predict Tetrahedral complexes :

(1) Bulky ligands (PPh_3) and WFL (Cl^-, F^- etc) favour the formation of Tetrahedral compound.

(2) Lower O.N of central atom favours the formation of tetrahedral complexes.

(3) d^{10} conf^n. of central atom with CN = 4, always Tetrahedral (sp^3)

d^0 also forms tetrahedral complex (d^3s)

V. Imp eg of tetrahedral complexes :

→ with O^{2-} ligand, Cr, V, Ti, Fe form tetrahedral complexes in CN = 4

$TiCl_4$, VO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, FeO_4^{2-}, MnO_4^-, MnO_4^{2-}

Tetrahedral complexes.

e.g with (PPh_3) bulky ⊛ and halido (F^-, Cl^- etc)

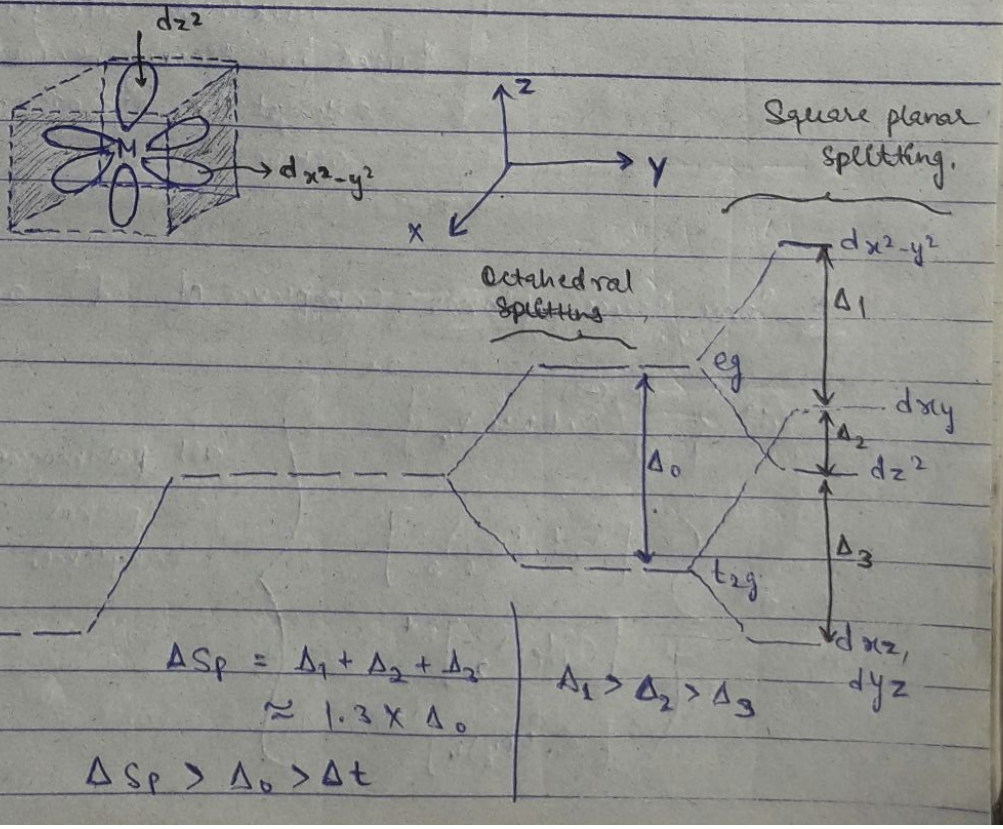
$[MnCl_4]^{2-}$, $[Co(SCN)_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$

$[Cu(CN)_4]^{3-}$, $[Zn(CN)_4]^{2-}$, $[NiCl_4]^{2-}$

$[NiCl_2(PPh_3)_2]$, $[Ni(CO)_4]$

} Tetrahedral complexes.

(b) Square planar Splitting (CN = 4)



$\Delta Sp = \Delta_1 + \Delta_2 + \Delta_3$

$\simeq 1.3 \times \Delta_0$

$\Delta Sp > \Delta_0 > \Delta t$

$\Delta_1 > \Delta_2 > \Delta_3$

V.Imp * Guidelines to predict square planar complex :

→ Mainly d^8 confn (and few cases of d^7 and d^9) shows square planar complexes in presence of SFL. The reason for d^8 showing sq. planar complex is high CFSE due to filling of e^- in lower energy orbitals $d_{yz}, d_{zx}, d_{z^2}, d_{xy}$

→ $3d^8$

↓

e.g Ni^{2+}

(Shows sq. planar complex with SFL)

eg. $[Ni(dmg)_2]$, $[Ni(CN)_4]^{2-}$,

$4d^8$ & $5d^8$

V.Imp Always form sq. planar complex (in CN = 4) whatever be the ligand.

e.g Ag^{3+}, Au^{3+}, Pd^{2+}, Pt^{2+}, Rh^{+}, Ir

↑ $4d^8$ ↑ $5d^8$ ↑ $4d^8$ ↑ $5d^8$ ↑ $4d^8$ ↑ $5d$

eg. $[\overset{(+3)}{Ag}F_4]^-$, $[AuCl_4]^-$, $[Pt(en)_2]^{2+}$

$[RhCl(PPh_3)_3]$, $[PtCl_4]^{2-}$

↑ Wilkinson catalysts (used in homogeneous catalyst in hydrogenation of alkene)

All Sq. planar complexes.

→ Some Square planar Complexes of d^7 and d^9 conf^n.

d^9 { $[\overset{(+2)}{Cu}(NH_3)_4]^{2+}$

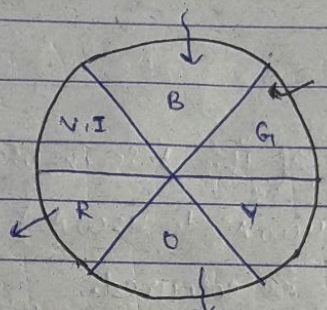
d^7 { $[Co(dmg)_2]$, $[Co(en)_2]^{2+}$, $[Co(Py)_4]^{2+}$

} all paramagnetic Sq. planar Complexes.

* Application of CFT :

① Colour of coordination compound :

→ A compound is coloured when it absorbs one of the wavelength of visible light (4000A° to 7500A°).
The colour visible to us is the colour of transmitted or reflected light (called complimentary light)



Complimentary colour circle.

if green light is absorbed then Red will the observed colour of compound. and vice-versa.

→ If a compound absorbs light other than visible portion then it will appear white (or colourless).

→ In general, it is observed that diamagnetic substance are generally white and paramagnetic (or having one or more unpaired e^-) are found to be coloured [However, it is not rule]

eg. Q. which is expected to be coloured ?

A. $ZnCl_2$ B. $MgSO_4$

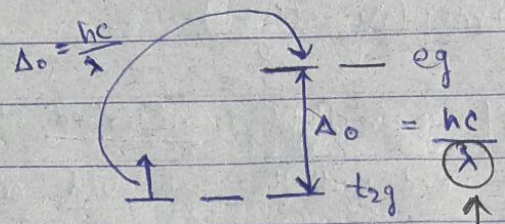
C. $AgCl$ D. $[Ti(H_2O)_6]Cl_3$

$[Ti(H_2O)_6]Cl_3$ → ~~Purple~~ compound.
Violet

→ Colour of d-block compounds is mainly due to d-d transition (expect d^0 and d^{10})

e.g $[Ti(H_2O)_6]Cl_3$ → Purple / Violet

↳ $3d^1 \Rightarrow t_{2g}^{1,0,0}, eg^{0,0}$



d-d transition

If this λ is in visible range (4000 A° to 7500 A°) then compound will be coloured.

Imp **NOTE** (1) In absence of ligand, compound may not show colour.

eg. $[Ti(H_2O)_6]Cl_3$ → Violet

↓ Δ (on heating H_2O is removed)

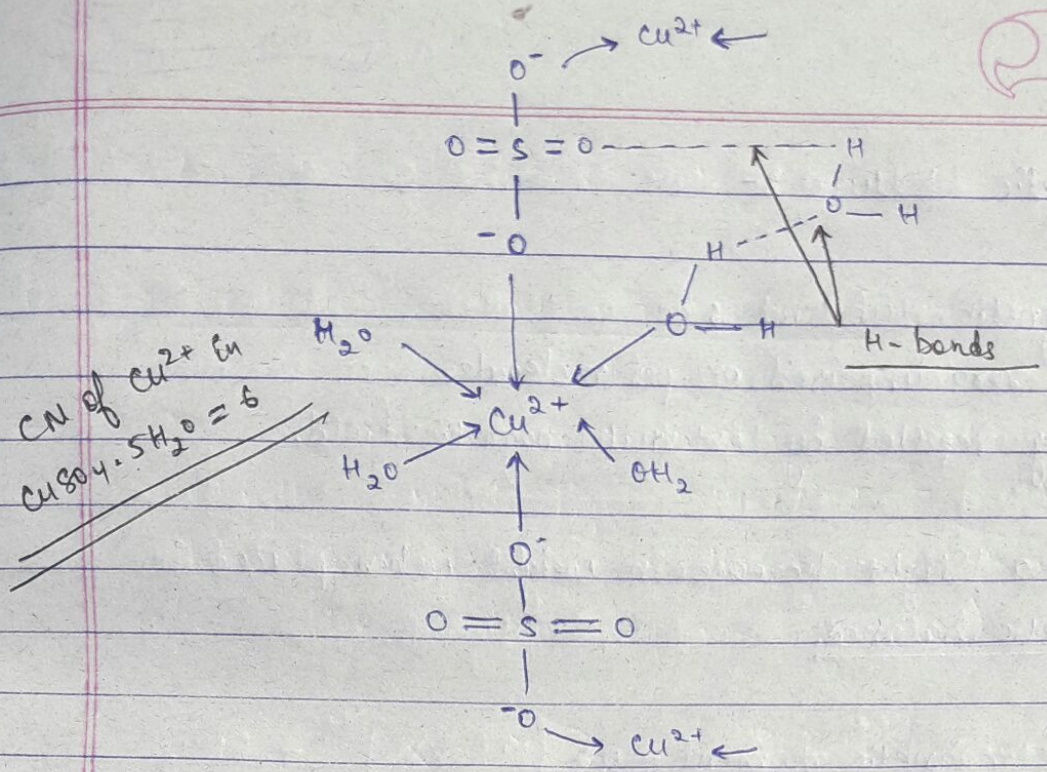
Colourless ($TiCl_3$)

→ $CuSO_4 \cdot 5H_2O(s)$ → Blue Solid

↓ Δ

Anhy. $CuSO_4$ (white)

v. imp IIT $4H_2O$ are directly bonded with Cu^{2+} through covalent (or coordinate) bonds and 5th H_2O is H-bonded.



(2) Many compounds including d^0 and d^{10} conf^n. show intense colours due to <u>charge transfer spectra.</u>

(i) Charge (or electron) transfer from L to M

(Purple) (orange) (orange)

↳ $KMnO_4$, ~~KB~~ $K_2Cr_2O_7$, SnI_4, Brown ring complex.

↳ O^{2-} to Mn

(CTLM) .

O^{2-} to Cr^{6+}

I^- to Sn^{4+}

$[Fe(H_2O)_5(NO^+)]^{+1}SO_4$

(ii) From M to L

eg. $[Fe(CO)_5]$, $[Cr(\eta^6-C_6H_6)_2]$, $[Fe(\eta^5-C_5H_5)_2]$

↓ due ~~to~~ is CTML

(2) Magnetic Nature :-

(a) Diamagnetic substance :

→ have zero unpaired e^- per molecule.

→ weakly repelled by external magnetic field.

imp → Show a slight decrease in weight when placed in magnetic balance.

→ Spin magnetic moment = 0

eg. $[Zn(NH_3)_4]SO_4$, $[Cd(CN)_4]^{2-}$, $[Sc(H_2O)_6]^{3+}$

(b) Paramagnetic compounds :

→ have 1 or more unpaired e^- per molecule

→ weakly attracted in magnetic field.

→ Show a slight increase in weight when placed in magnetic balance.

→ Spin magnetic moment $\neq 0$.

Spin magnetic moment $= \sqrt{x(x+2)}$ B.M

where x = No. of unpaired e^-

eg. $[Cu(NH_3)_4]^{2+}$, Brown Ring Complex $[Fe(H_2O)_5(NO^+)]SO_4$

eg. $[COF_6]^{3-}$

$3d^7$, $t_{2g}^{2,2,1}$, $eg^{1,1}$, sp^3d^2

$(x = 3)$

Paramagnetic

③ Stability of complex compounds :-

Thermodynamic Stability

Higher is the formation constant (k_f) of complex, greater will be its thermodynamic stability.

eg. $M + L \rightleftharpoons ML, k_{f_1}$

$ML + L \rightleftharpoons ML_2, k_{f_2}$

$ML_2 + L \rightleftharpoons ML_3, k_{f_3}$

$ML_3 + L \rightleftharpoons ML_4, k_{f_4}$

Kinetic Stability

Labile ligand/complex (or Reactive complex) ⇓

Labile : easily replaced

→ Reactive complexes where ligands are labile and can be easily substituted by other ligand.

→ Ea is low for labile ligands

Inert ligand/complex (Stable)

→ Ea is high.

$M + 4L \rightleftharpoons ML_4$,

$\beta_4 = \underbrace{k_{f_1} \times k_{f_2} \times k_{f_3} \times k_{f_4}}_{\text{Stepwise formation constant}}$

β_4 : Overall formation constant (k_f) or Stability constant ($k_{stability}$)

→ $ML_4 \rightleftharpoons M + 4L$, $k_{instability} = \frac{1}{\beta_4}$ or $\frac{1}{k_f}$

$k_{instability}$: Instability constant.

In general, $k_f \uparrow$, Thermodynamic Stability $\uparrow$

* Entropic effect (or Chelate effect):

→ Complex having bidentate or polydentate ligands are highly stable. Greater are the number of 5 or 6 membered chelating rings, greater will be the stability of complex.

→ It is due to entropy increase by large amount when monodentate ligands are replaced by bidentate ligands.

eg. $\underbrace{[M(NH_3)_6]^{x+} + 3en}_{4 \text{ molecules}} \longrightarrow \underbrace{[M(en)_3]^{x+} + 6NH_3}_{7 \text{ species}}$

ΔS = highly +ve

$\Delta G = \Delta H - T\Delta S$

ΔG : -ve highly

ΔH : -ve

$T\Delta S$: +ve

→ For the above rxn. ΔS is highly +ve and makes ΔG highly -ve and therefore this reaction is controlled by entropy change and hence called

ENTROPIC EFFECT

or Chelate effect.

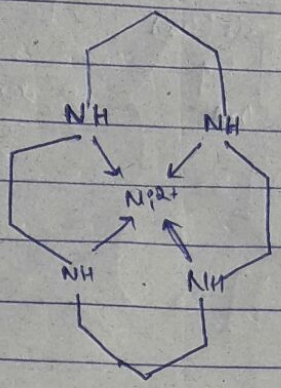
⇒ $[M(en)_3]^{x+}$ is more stable thermodynamically than $[M(NH_3)_6]^{x+}$

Note: It has been observed that polydentate or multidentate ligands having cyclic rings form highly stable complexes. Such ligands are called macrocyclic ligands and the effect is known as macrocyclic effect.

(It is an extension or application of entropic effect)

eg. Cyclam, $(NHCH_2CH_2NHCH_2CH_2CH_2)_2$
Tetradentate

macrocyclic ligand



Highly Stable

Note: (1) M^{3+} forms more stable complex than M^{2+} with same type and same no. of ligands.

$$\rightsquigarrow \left[Co(NH_3)_6\right]^{3+} > \left[Co(NH_3)_6\right]^{2+}$$

more stable complex

Reason: Co^{3+} is smaller in size than Co^{2+}

(2) M^{2+} ions of 3d series

$Ti^{2+}, V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$

↳ Stability M^{2+} complex with same no. and same type of ligands can be compared on the basis of size of M^{2+}.

Size of M^{2+} ↓, Stability ↑

$$Ti^{2+} < V^{2+} < Cr^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+} \longrightarrow$$

order of Stability of M^{2+} complexes.

[Irving - William series]

V. Imp

(3) Co^{2+} ion in aqueous medium is more stable than Co^{3+} (aq)

However Co^{3+} forms very high stable complexes with SFL due to high CFSE released.

$$[Co(H_2O)_6]^{2+} + NH_3(aq) \xrightarrow[\text{air } (O_2)]{\text{atmospheric}} [Co(NH_3)_6]^{3+} + 6H_2O$$

O_2: O.A

$[Co(NH_3)_6]^{3+}$: more stable complex.

$[Co(NH_3)_6]^{3+}$

$3d^6$ $\left(t_{2g}^{2,2,2}, eg^{0,0} \right)$

$$CFSE = -2.4\Delta_0 + 2P$$
$$= -ve \text{ (highly)} \quad \{\Delta O >> P\}$$

* Thermodynamic stability of complex depends on many factors like -

(1) Bond Strength between ligand & central atom.
(2) Entropic effect (or Chelate effect)
(3) High CFSE released.

* Isomerism in Coordination Compounds :-

- Structural Isomerism (connectivity of ligand is different)
- Stereoisomerism (connectivity is same, but orientation is different)
  - Geometrical
  - Optical.

① Structural Isomerism :

(i) Ionisation Isomerism :

→ Such isomers produce different ions in aq. solution.

→ This arise when a ligand can be exchanged with counter ions.

eg. $[Co^{(+3)}(NH_3)_4Br_2]Cl$

$[Co(NH_3)_4BrCl]Br$

} Ionisation isomers.

(ii) Hydrate Isomerism / ~~Solvent~~ + Solvate Isomerism :

→ Water ligand can be exchanged with counter ions.

→ Such isomers show different behaviour towards conc. H_2SO_4 or a dehydrating substance.

eg. $[Cr(H_2O)_6]Cl_3$

$[Cr(H_2O)_5Cl]Cl \cdot H_2O$, $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

} Hydrate isomers.

(iii) Linkage isomerism :

→ This arise when an ambidentate ligand is present in the complex.

eg. $[Cr(H_2O)_4(SCN)(NO_2)]Br$ } SCN, NO_2 ambidentate ligand

$[Cr(H_2O)_4(NCS)(NO_2)]Br$

$[Cr(H_2O)_4(NCS)(ONO)]Br$

$[Cr(H_2O)_4(SCN)(ONO)]Br$ } linkage isomers.

(iv) Coordination isomerism :

→ This arise when both cationic and anionic parts of compound are complex part.

→ Such isomers are formed by exchanging either central atoms or ligands.

eg. $[\overset{(+3)}{Co}(NH_3)_6]^{3+}[\overset{(+3)}{Cr}(NO_2)_6]^{3-}$

$[Co(NH_3)_5(NO_2)][Cr(NH_3)(NO_2)_5]$

$[Co(NH_3)_4(NO_2)_2][Cr(NH_3)_2(NO_2)_4]$

$\Rightarrow$ ~~$[Co(NH_3)_3(NO_2)_3][Cr(NH_3)_3(NO_2)_3]$~~

does not exist

$[Cr(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$

$[Cr(NH_3)_5(NO_3)][Co(NH_3)(NO_2)_5]$

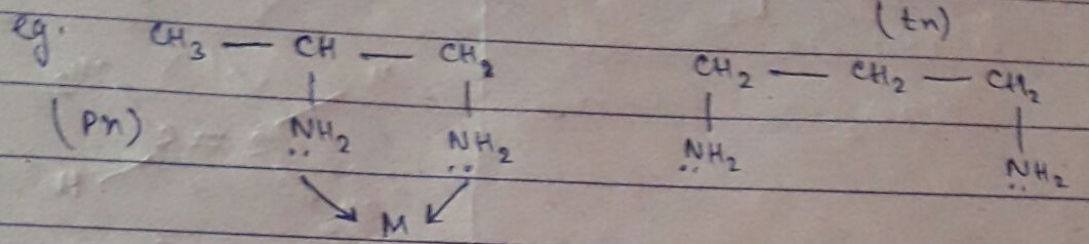
PTO →

$[Co(NH_3)_6][Co(NO_2)_6]$

(Total 5 coordination isomers)

(v) Ligand isomerism :

→ Ligand itself shows isomerism.

eg. 

(vi) Polymerisation isomerism :

→ It is not the true isomerism as molecular weight of isomers differ.

→ It is a special type of coordination isomerism in which isomers differ in mol. wt.

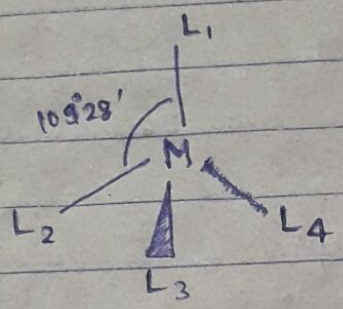
eg. $[Co(NH_3)_4(NO_2)_2][Co(NH_2)_2(NO_2)_4]$ → 2M

$[Co(NH_3)_5(NO_2)][Co(NH_3)_2(NO_2)_4]$ → 3M

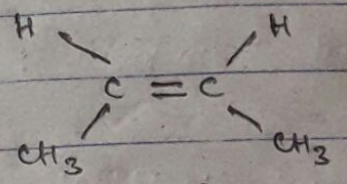
Polymerisation isomerism.

* Stereoisomerism : → Geometrical
→ optical

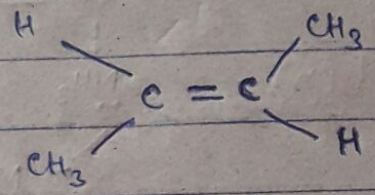
CN = 4 (Tetrahedral complexes)



Organic Chemistry



cis-isomers



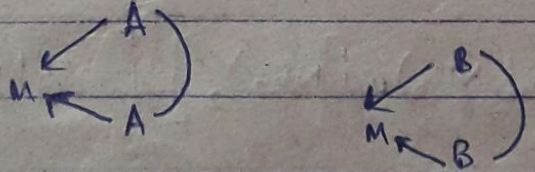
trans isomers.

V. Imp Tetrahedral complexes do not show geometrical isomerism but may show optical isomerism.

M → Central atom

a, b, c, d → Monodentate ligands

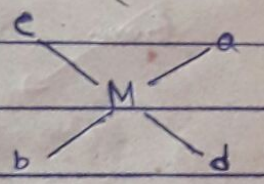
AA, BB, CC → Symmetrical bidentate ligands.
(eg. en, ox^{2-}, urea)



AB, CD, EF → Unsymmetrical bidentate ligands.
(eg. gly^-, pn, tn, $dmgH^-$ etc)

	Optical Isomerism
Ma_4	
Ma_3b	×
Ma_2b_2	×
Ma_2bc	×
→ Mabcd	×
$M(AA)b_2$	✓
$M(AA)bc$	×
$M(AB)c_2$	×
→ $M(AB)(cd)$	×
$M(AA)_2$	✓
$M(AA)(BC)$	×
→ $M(AB)_2$	×
→ $M(AB)(CD)$	✓
	✓

* CN = 4 (Square Planar Complex):



Sq. planar Geometry

→ Sq. planar complexes do not show optical isomerism (due to the presence of plane of symmetry) but may show geometrical isomerism.

Complex	Geometrical Isomerism
Ma_4	×
Ma_3b	×
→ Ma_2b_2	✓ (2)
→ Ma_2bc	✓ (2)
→ Mabcd	✓ (3)

$M(AA)b_2$ ✗

→ donors of bidentate ligands always occupy cis-position

$M(AA)bc$	✗
$M(AB)(AC)c_2$	✗
$M(AB)(cd)$	✓ (2)
$M(AA)_2$	✗
$M(AA)(Bc)$	✗
$M(AB)_2$	✓ (2)

* CN = 6 (octahedral complexes):

→ Octahedral complexes may show geometrical as well as optical isomerism.

Complex	G. I	Enan.
Ma_6	✗	
Ma_5b	✗	
Ma_4b_2	✓ (2)	
Ma_4bc	✓ (2)	
Ma_3b_3	✓ (2)	

→ If outer of 8 triangular faces in octahedral structure, two triangular faces have vertices occupied by same ligands then the isomer is called facial (fac-isomer).
Else it is called meridional (mer-isomer).

Ma_3b_2c ✓(3)

Ma_3bcd ✓(4) Total Stereoisomers = 3+2 = 5

gmf $Ma_2b_2c_2$ ✓(5) Total stereo. = 4+2 = 6

Ma_2b_2cd ✓(6) → 2 active, 4 inactive Total stereo. = 4+4 = 8

Ma_2bcde ✓(9) → 6 active, 3 inactive Total stereo. = 3+12 = 15

$Mabcdef$ ✓(15) all active Total stereo = 30

$M(AA)b_4$ ×

$M(AA)b_3c$ ✓(2)

gmf $M(AA)b_2c_2$ ✓(3) Total Stereo = 2+2 = 4

gmf $M(AB)c_2d_2$ ✓(4) Total Stereo = 2+4 = 6

gmf $M(AA)_2b_2$ ✓(2) Total stereo = 1+2 = 3

gmf $M(AA)_2bc$ ✓(2) Total Stereo = 1+2 = 3

V.gmf IIT-Adv. $[M(AB)_2c_2]$ ✓5 Total Stereo = 2+6 = 8

(AB)(AB)(CC)] inactive
(AA)(BB)(CC)]

(AC)(AC)(BB)]
(BC)(BC)(AA)] active
(AB)(AC)(BC)]

Total Stereo = 2 (d & l)

* $M(AA)_3$ ×

(AA)(AA)(A) * $[M(AA)_3]$ does not show any geometrical isomerism but it shows optical isomers

Qmq $[M(AB)_3]$ ✓(2)

Total stereo = 4

(AB)(AB)(AB) } Both optically active
(AA)(BB)(AB) }

Qmq $[Co(EDTA)]^-$ → optically active

(*) SYNERGIC BONDING :-

→ Ligands → classical ligands : LP donors (No back bond)
eg. H_2O, NH_3, OH^-, F^-, NH_2^- etc.

→ Non-classical ligands :
L.P donor or π-e⁻ density donor and π-acid acceptor as well
(can form π-back bond)

CO, NO, N_2, PPh_3, PR_3, PF_3, PCl_3, etc

C_2H_4, $C_5H_5^-$, C_6H_6

M ⇄ L (π, σ)

π-e⁻ from metal are accepted in π* MO (π ABMO)

↑ accepted in d orbitals

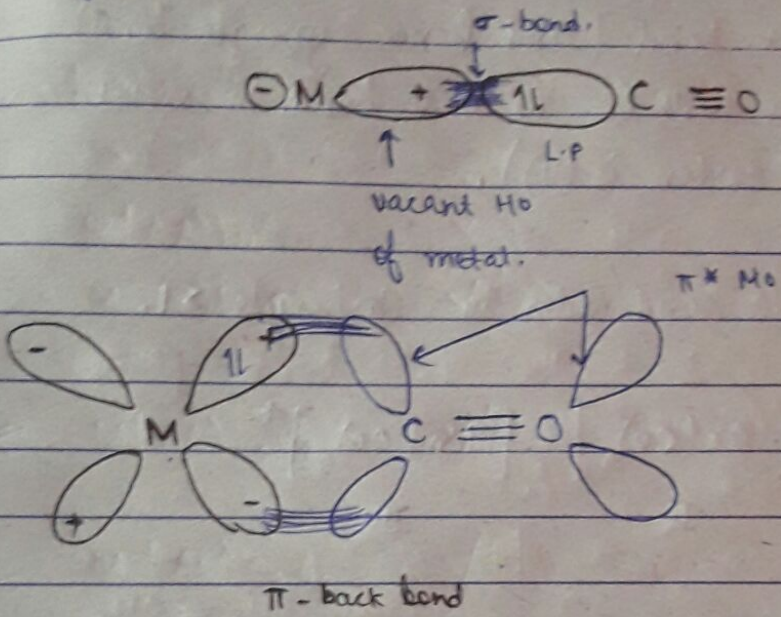
M ⇄ L (π, π)

↑ (Bond is σ)

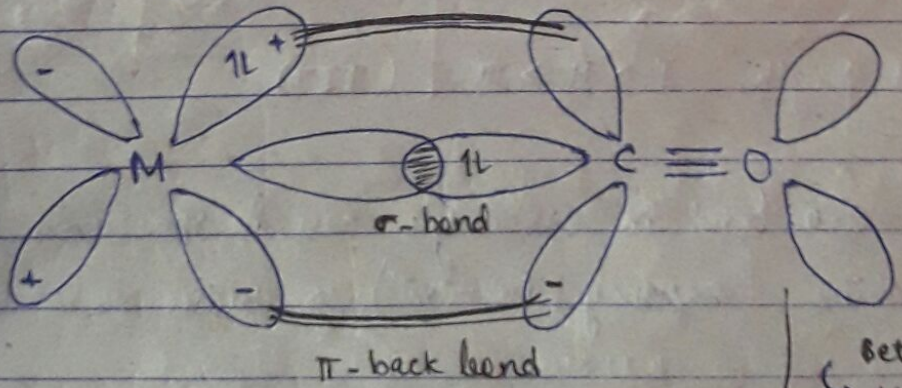
* Bonding in Carbonyl Compounds : (Synergic bonding)

→ CO donates a L.P to vacant hybrid orbital of central atom and simultaneously accept L.P from d-orbital of metal to its vacant π ABMO forming π-back bond along with σ-bond.

→ Together σ and π-bonds is called synergic bond.



→ Seeing collectively, the synergic bond is :-



→ Why it is called synergic bond ?

∋ Synergise means Strengthening

↳ Better donor
high e⁻ density or low EN.

↳ Better acceptor
low e⁻ density or high EN.

→ π - back bond from metal to vacant orbital of CO makes CO electron rich or makes it better L.P donor.

Similarly, σ - donation from CO to metal makes e^- rich (EN of metal ↓), so metal's LP donating tendency to CO increases.

→ Synergising effect.

→ Stronger is π - back bond (and hence synergic bond) i.e M-C bond, weaker will be the C-O bond in metal carbonyls. (Because valency of carbon is (4)).

Remember that M-C bond order in Carbonyls > 1.

eg. $[V(CO)_6]^-$, $[Cr(CO)_6]$, $[Mn(CO)_6]^+$

I II III

⇒ M-C bond order , I > II > III

⇒ C-O bond order , I < II < III (IIT)

⇒ C-O bond length, I > II > III (IIT)

→ Strength of C-O bond in carbonyls can be measured in terms of stretching frequency (in cm^{-1}) or wave number.

$E = h\bar{\nu}$

↑

Streching frequency ∝ B.O or bond strength.

→ PF_3 is also a strong π-acid ligand.
(nearly same strength as that of CO)

$PF_3 > PCl_3 > PBr_3$
$PF_3 > PPh_3 > PH_3$
} decreasing tendency to accept l.p from metal via π-back bond.

↑
PH_3 forms a very weak synergic bond (π-back bond tendency is very low)

Q. If PF_3 is better or stronger π-acid ligand than CO, then compare M-C and C-O bond order among-

$[Ni(CO)_4]$ and $[Ni(CO)_3(PF_3)]$

Soln $[Ni(CO)_4] < [Ni(CO)_3(PF_3)]$

↑ Stronger M-C bond and weaker C-O bond.

↑ Stronger C-O bond & weaker M-C bond

Q Compare $[Ni(CO)_3(PF_3)]$ and $[Ni(CO)_3(PMe_3)]$

Soln $[Ni(CO)_3(PF_3)]$ $[Ni(CO)_3P(Me)_3]$

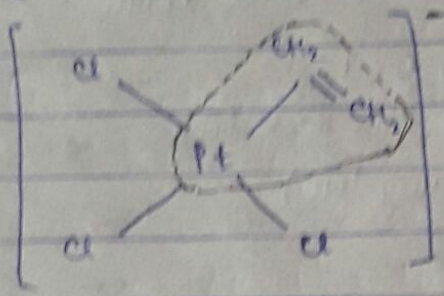
↑ ~~Strong~~ weaker M-C bond
Stronger C-O bond

↑ Stronger M-C bond
weaker C-O bond

* Synergic bonding in Zeise's Salt :

Zeise's Salt : $K[PtCl_3(\eta^2 - C_2H_4)]$

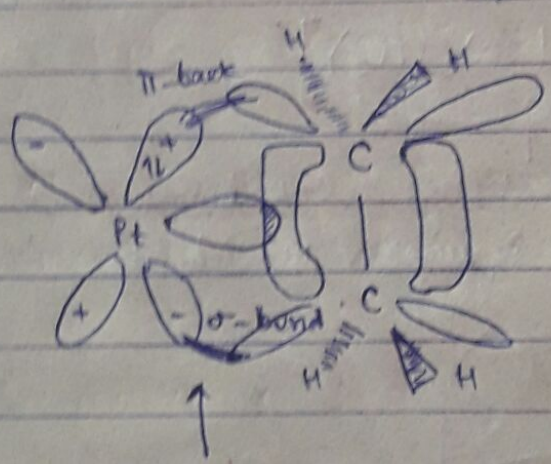
(Sq. planar complex about Pt atom, dsp^2)



anion of zeise's salt

→ C-C bond axis is ⊥ to the Pt-Cl bonds plane

→ C_2H_4 is a π-acid acceptor.



Free $CH_2 = CH_2$

↑

C-C bond length = x pm

$y > x$ Imp

Pt-C bond is synergic bond.

→ π-back bond is formed between fully filled d-orbital of Pt atom and vacant π*MO of C_2H_4 ligand

→ In carbonyl compounds,

Free CO(g). C-O bond length

≃ 1.128 A° (Remember)

⇒ In carbonyl complex, eg. $[Fe(CO)_5]$

↑ C-O bond length ≈ 1.150 A°
(slightly increase)

IIT Q. In free CO(g), C-O bond length is 1.128 A°, then C-O bond length in $[Fe(CO)_5]$ is :-

(A) 1.128 A° (B) 1.12 A°

(C) 1.15 A° (D) 1.172 A°

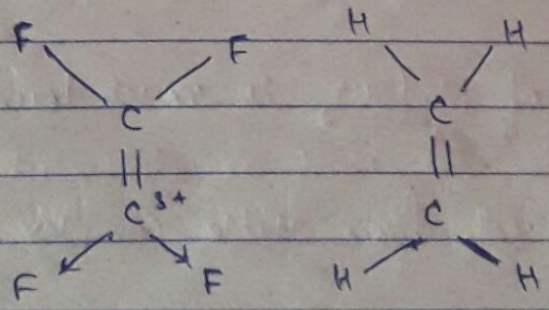
Imp →

$CH_2 = CH_2$ is a π-acid ligand

→ If H is replaced by highly EN element then ability to accept L.P from metal is drastically increased.

eg. $C_2(CN)_4 > C_2F_4 > C_2H_4$

decreasing Strength of π-acid acceptor.



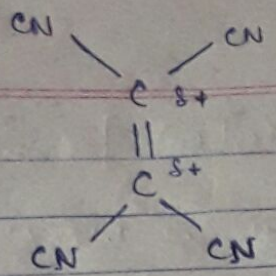
NSEC - 2019 Q.

In complex salt $K[PtCl_3(\eta^2 - C_2R_4)]$ if R can be H, F, CN, then in which complex C-C bond will be longest?

A. C_2F_4 B. C_2H_4

C. $C_2(CN)_4$ D. $C_2(CH_3)_4$

Soln:



(*) Applications and Importance of Coordination Compounds -

(1) Sodium Salt of EDTA is used in estimation of hardness of waters to determine / estimate Ca^{2+} and Mg^{2+}

→ At pH = 10 (buffered with NH_3 / NH_4^+)
Amount of Ca^{2+} and Mg^{2+} is estimated using EDTA because Ca^{2+} / Mg^{2+} both form stable complex with EDTA

$$[Ca(EDTA)]^{2-}, \quad [Mg(EDTA)]^{2-}$$

$$K_f, Ca(EDTA)^{2-} > K_f, Mg(EDTA)^{2-}$$

→ At pH = 12, Mg^{2+} can be removed from hard waters having Mg^{2+} and Ca^{2+} as $Mg(OH)_2(s)$

Solubility of $Mg(OH)_2$ is much lower than $Ca(OH)_2$.

Q which does not form stable complex with EDTA ?

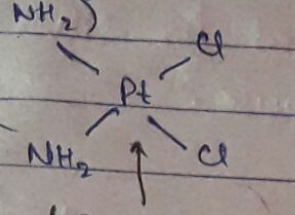
(A) Co^{3+}
(B) Be^{2+}
(C) Ca^{2+}
(D) Mg^{2+}

→ Be^{2+} can't have CN more than 4.

imp
NSEC

→ Calcium salt of EDTA is used in treatment of lead poisoning.

$$Pb^{2+} + [Ca(EDTA)]^{2-} \longrightarrow [Pb(EDTA)]^{2-} + Ca^{2+}$$

→ Cis-platin () is an anti-cancer drug.

(Sq. planar complex)

imp
→ In metallurgy : (Mond's process)

To purify impure Ni,

$$\underset{\text{(Impure)}}{Ni} + CO(g) \xrightleftharpoons{\approx 50^\circ C} Ni(CO)_4(g)$$

$$Ni(CO)_4(g) \xrightarrow{\approx 200^\circ C} Ni(s) + 4CO\uparrow$$

(Pure Nickel)

* For extracting Ag / Au from native ore of Ag / Au.
(Mc Arthur Forest process)

$$\underset{(Ag/Au)}{M}(s) + O_2 + NaCN(aq) \longrightarrow \underset{\text{Stable complex}}{[M(CN)_2]^{-}} + OH^-$$

(M = Ag/Au)

$$[M(CN)_2]^- \xrightarrow{Zn(s)} Ag/Au + [Zn(CN)_4]^{2-}_{(aq)}$$

(Pure)

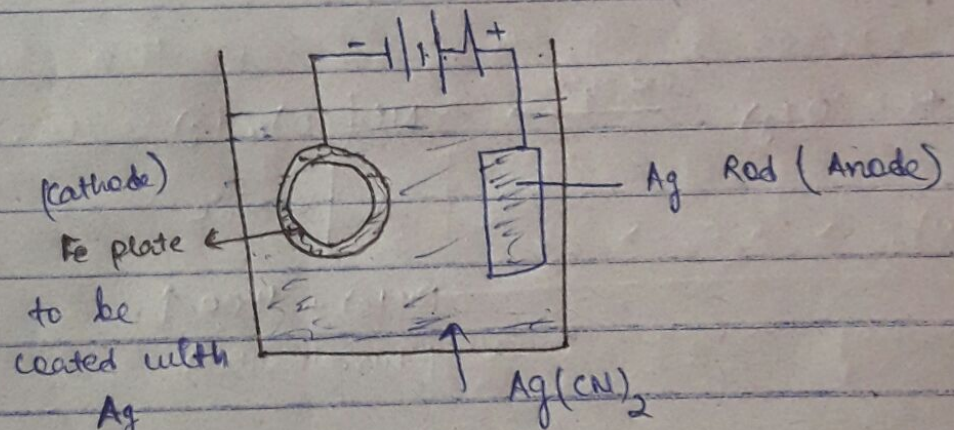
Ans → Gold plating or Silver plating :-
Table ware (spoon, glass / plates) are silver coated.

KCN / AgCN is used as electrolyte

→ Cyanide solution is used for silver coating on an article (spoon) on cathode because :

→ $Ag(CN)_2^-$ complex provides slow Ag^+, so a very fine coherent / uniform coating is formed on spoon.

→ CN^- corrodes Ag / Au anode and helps in oxidation at anode.



* $AgNO_3$ is not used as electrolyte, cyanide is preferred.

→ Hypo is used as fixer solution to remove unused coating of AgBr

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$$

(fixer solution)

→ Chlorophyll → contains Mg.
(a green pigment in plants)

* B-12 Complex → contains Cobalt (Co)

* Haemoglobin → contains Fe

* Read NCERT without fail

END :-)